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HIS LATE HIGHNESS MAHARAJA
SRI KRISHNARAJA WADIYAR BAHADUR, G.C.S.I., G.B.E.
MYSORE
(4TH JUNE 1884 — 3RD AUGUST 1940)

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SRI KRISHNARAJA WADIYAR BAHADUR
G.C.S.I., G.B.E.

(4th June 1884—3rd August 1940)

THE sudden death of His Highness Sir Sri Krishnaraja Wadiyar Bahadur, the late Maharaja of Mysore, has come to us as a rude shock, and leaves his subjects with a sense of acute personal loss.

It is impossible in the short space at our disposal to give an adequate account of his long and illustrious reign in the course of which he built for Mysore a reputation abroad of being the most progressive State in India. His great personal qualities endeared him to all those who came in contact with him. His simplicity of life, religious feeling, humanitarian outlook, great sense of duty and above all his extreme devotion to the welfare of his subjects were known by repute to people throughout India who had no connection with the State of Mysore. He will always be cited as an example of what a great Ruler should be.

But posterity will perhaps remember him above all for having begun and carried through to a great extent the Industrialization of the State of Mysore. He was a great patron of the Arts and Sciences. To him is largely due the establishment of the Indian Institute of Science in Bangalore, made possible by the generous grant of a vast extent of land and a handsome gift of money supplemented by an annual contribution. He laid the foundation stone of the Institute in the year 1911. The Indian Academy of Sciences, in particular, owes a deep debt of gratitude to His Highness and to the equally far-sighted Dewan, Sir Mirza M. Ismail, for a generous annual grant to the Academy and the gift of a large extent of land in a commanding situation in Bangalore for the

purpose of building a permanent home for the Academy. There is no space to enumerate the very material patronage given by him to every Scientific and Educational Institution, Hospitals, Agricultural Projects and Rural Development Centres.

His Highness's love of the Arts, in particular, Music, is equally well known. Through it was made possible the enlightened policy of the present Dewan of beautifying the State of Mysore by the making of large parks, and the construction of handsome public buildings so that the subjects of Mysore and especially the rising generation may develop in them a sense of beauty, orderliness and pride in their State such as is found in Europe.

As President of the Indian Academy, I most respectfully beg to convey the condolences of the Fellows of the Indian Academy of Sciences to Her Highness the Dowager Maharani of Mysore, to His Highness Sri Jayachamaraja Wadiyar and the other members of the Royal Family for the sad bereavement they have sustained.

C. V. RAMAN.

REFLECTION OF X-RAYS WITH CHANGE OF FREQUENCY

Part IV. Rock-Salt

By Sir C. V. Raman and Dr. P. Nilakantan
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Received August 1, 1940

1. Introduction

The second and third papers of this series (Raman and Nilakantan, 1940) described an experimental study of the phenomena observed when X-rays incident on a crystal excite the characteristic vibrations of its lattice structure, resulting in a reflection of the X-rays with altered frequency. The experimental results disclosed remarkable differences between the behaviour of the two crystals studied, namely, diamond and sodium nitrate, in respect of the details of the phenomenon, *viz.*, the geometric law of the modified reflection, the range of incidences over which it may be observed with any particular crystal spacing, the definition which it exhibits at various incidences, the influence of temperature on its intensity, and so forth. These observations indicated the importance of studying the phenomena with a variety of other substances with a view to correlating the results with the crystal structure and infra-red spectrum of the substance. Such a correlation should be possible in the light of the quantum-mechanical theory of X-ray reflection which has been developed and of which the first part has been published in these *Proceedings* (Raman and Nath, 1940, I). The present investigation deals with the case of rock-salt, which is of special interest in view of the simplicity of its structure, and has resulted in an advance of our knowledge of the subject in several directions.

2. Lattice Structure and Lattice Vibrations

The structure of rock-salt was one of the earliest to be established by the X-ray method. As is well-known, the crystal is built up of sodium and chlorine ions grouped round each other and forming two similar interpenetrating face-centred cubic lattices. The crystal planes which contain equal numbers of sodium and chlorine ions have the lattice spacing halved and give only the reflections of even orders, while the others in which layers of sodium and chlorine ions alternate exhibit the full lattice spacings and

therefore give both odd and even order reflections. In the X-ray reflections of even orders given by both types of spacings, the sodium and chlorine ions co-operate and therefore enhance the intensity, while in the reflections of odd orders given by the undivided spacings, they subtract from each other's effects. The reflections of even and odd orders therefore form two different sequences in one of which the intensity is large and in the other it is small. In both sequences, the intensity falls off as the spacing diminishes (Bragg, James and Bosanquet, 1921). Table I shows all the reflections observed with rock-salt of which the intensity is 5 per cent. or more of the reflections given by the cleavage faces. The figures for the (100), (110) and (111) reflections are taken from the authors quoted, and those for the 210 (2), 211 (2) and 221 (2) reflections are obtained by interpolation from their curve.

TABLE I

Spacings and Reflection Intensities

Halved Spacings			Full Spacings		
Miller indices	Spacings in A.U.	Reflection intensity	Miller indices	Spacings in A.U.	Reflection intensity
100 (2)	2·814	100	111 (1)	3·250	9
110 (2)	1·990	50	111 (2)	1·625	33
100 (4)	1·407	20			
210 (2)	1·259	15			
211 (2)	1·149	12			
110 (4)	0·995	6			
221 (2)	0·938	5			
100 (6)	0·938	5			

The reflecting power of rock-salt for infra-red radiation shows a large increase over the region of wave-lengths from 40 μ to 80 μ, the curve exhibiting a broad maximum at 52 μ. The absorption of infra-red radiation by the crystal is very strong over the whole of this region, but by using a thin layer, it is possible to resolve the transmission curve and observe the principal maximum of absorption at 61 μ and feebler subsidiary maxima at 51 μ and 41 μ (Barnes, 1932). It is obvious that an oscillation of the two interpenetrating lattices of sodium and chlorine atoms with respect to each other would give rise to a large electric moment along the direction of movement. Such

an oscillation would be strongly active in the infra-red, and the absorption maximum observed at 61 μ (164 cm.$^{-1}$) may therefore reasonably be identified with it. Symmetry considerations indicate that the same oscillation would be inactive in light-scattering. Actually, as has been shown by Fermi and Rasetti (1931), rock-salt exhibits in a very strongly exposed spectrum of light-scattering, a band covering the region of frequency shift from 160 cm.$^{-1}$ to 365 cm.$^{-1}$ with a series of intensity maxima clearly visible within this range. This has been explained by Fermi and Rasetti as a second-order effect. The lower frequency limit of the band, it will be noticed, is about the same as the characteristic infra-red absorption frequency, and the upper limit approximately the octave of it. In view of these facts, it appears justifiable to conclude that the principal optical frequency of the rock-salt structure is 164 cm.$^{-1}$ and that this frequency corresponds to a movement of the two interpenetrating lattices with respect to each other.

Owing to the cubic symmetry of the crystal, the oscillation referred to above would be triply degenerate, that is, may take place in any arbitrary direction with the same frequency. It is also evident that the oscillation would influence the structure amplitude of all the crystal spacings except such as happen to be actually parallel to it. Considering the lattice planes containing equal numbers of sodium and chlorine ions, the average electron density exactly midway between such planes would be neither increased or decreased by an oscillation in which adjacent sodium and chlorine ions alternately approach and recede from each other. Nearer the planes, however, the electron density would be increased in one half of the oscillation and decreased in the other half, or *vice versa*. The wave-length of the oscillation of electron density would therefore be the same as the distance between such planes, and its time-period identical with that of the oscillation of the lattices. In the case of the planes which contain only sodium or chlorine ions alternately, the electron density midway between such planes is increased in one half of the oscillation and decreased in the other half, or *vice versa*. Here again, therefore, the wave-length of the oscillation of electron density is the same as the distance from one plane of atoms to the next of the same kind. In other words, the dynamic stratifications of electron density have their spacings halved or not halved, in the same way as the corresponding static periodicities.

The considerations set out above indicate that Table I which is a list of the spacings in rock-salt which give intense unmodified reflections would equally well represent a list of the spacings giving strong modified reflections as the result of the oscillations of the lattice structure. All the lattice planes except (111) should give the even order reflections only, and we may further

expect the intensity of these reflections to fall off in a regular sequence with the diminution of the crystal spacings in much the same way as for the unmodified reflections. The case of the (111) planes, however, requires special consideration. The static structure amplitude of these planes is greater for the second order than for the first, the intensities of these reflections being in the ratio 33 : 9. The characteristic vibration of the crystal structure would however influence the structure amplitude more for the first order than for the second order, the movements of the two interpenetrating lattices being in opposite directions. Accordingly, the intensity of the modified reflections of the first and second orders from the (111) planes should not exhibit such a large disparity as the unmodified reflections of these orders.

3. *Geometry of Modified Reflection*

The geometric relations entering in the modified reflection of X-rays have been discussed in detail on the basis of the quantum theory by Raman and Nath (1940) in a recent paper in these *Proceedings*. The results briefly stated are: the modified reflection appears in the plane of incidence of the X-ray beam on the crystal spacing under consideration; the glancing angles of incidence and reflection θ and ϕ respectively are, in general, not equal to each other, but satisfy the relation

$$2\,d \sin \tfrac{1}{2}(\theta + \phi) = n\,\lambda; \qquad (1)$$

the intensity of the reflection is greatest when $\theta = \phi$ and falls off when θ and ϕ diverge from each other, at first very rapidly, and later more slowly. These three results enable us readily to determine the general features of the modified reflections appearing in a Laue pattern for any stated orientation of the crystal.

Equation (1) indicates that *the angular separation between the incident beam and the modified reflection from any particular spacing is independent of the setting of the crystal*. Round the centre of the pattern (*viz.*, the point at which the incident beam meets the photographic plate), we draw a series of circles on the plate corresponding to this angular separation for each of the crystal spacings capable of giving modified reflections of sufficient intensity to be observed. It will be seen from equation (1) that the position of these circles on the plate would coincide with the rings in the powder-pattern of the crystal for the same plate distance. From the centre of the pattern, we then draw a set of radial lines on the plate such that each such line and the incident X-ray together define the plane of incidence of the latter on the particular crystal spacing under consideration. The points at which the circles and the radial lines intersect give the positions of the modified reflections. If the wave-length of the X-ray is changed,

the powder-diagram circles would expand or contract, and the modified reflections would therefore move in or out along the radial lines. The modified reflection of the white radiation present in the incident pencil would therefore appear as a radial streak on the same line as the spots due to the monochromatic rays.

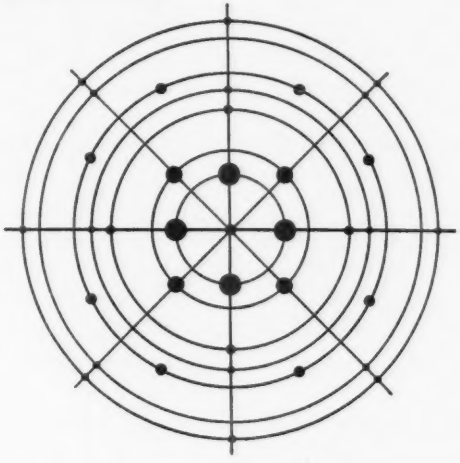

FIG. 1
Pattern of Modified Reflections: Direction of Incidence [100]

Since the angles θ and ϕ may have any values satisfying equation (1), it is not necessary for recording a modified reflection that the particular crystal plane should be in such an orientation as to give a Laue reflection observable on the plate. We may, for instance, have $\theta = 0$, in other words, the incident ray grazes the crystal plane, in which case the Laue reflection would be unobservable but the modified reflection would appear at an angle ϕ with the incident beam given by the relation

$$2\,d \sin \tfrac{1}{2}\phi = n\,\lambda \qquad (1a)$$

It may be remarked also that θ and ϕ need not be positive. One of them may be positive and the other negative, and the integer n which gives the order of the reflection may be either positive or negative. The range of admissible values of θ and ϕ and the permissible values of n are, however, limited by considerations of intensity. If θ and ϕ differ too widely, or if n be too large, the modified reflection may be unobservable. Figs. 1 and 2 represent the modified reflection patterns drawn in this way for the cases in which the incident X-ray beam traverses the [100] and [110] directions respectively within the crystal. The circles drawn in these figures are the Debye-Scherrer

rings for the crystal spacings listed in Table I. Since the 441 and 600 spacings are identical, there are only nine rings to be considered. In Fig. 1,

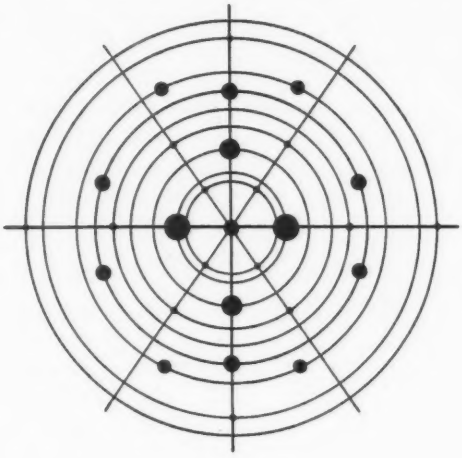

FIG. 2
Pattern of Modified Reflections: Direction of Incidence [110]

the 111 and 222 circles have been omitted, as the value of θ for these spacings would be too large for the corresponding modified reflections to be of observable intensity. They however appear in Fig. 2. In both of these cases, the incident X-ray grazes some of the planes giving the strongest modified reflections. For instance, a beam along [100] grazes the following planes: (001), (010), (011) and (01$\bar{1}$). A beam along [110] grazes the following planes: (001), ($\bar{1}$10), ($\bar{1}$11) and (1$\bar{1}$1). Accordingly, in these cases, the reflections by these planes appear in the directions given by the formula (1 *a*) and form an important feature of the observed patterns. Other reflections can also appear on the pattern if the orientation of the planes in question is not too remote from that necessary for a Bragg reflection. These have also been drawn in the figures.

It is interesting to consider in what way the pattern represented in Fig. 1, would be altered if the orientation of the crystal is altered, step by step, by rotating it about a suitable axis. The X-ray beam has initially the direction [100] within the crystal, and the latter is then rotated about a perpendicular direction, say [010], a few degrees at a time. By virtue of formula (1), the modified reflections would in such a case continue to lie on their respective circles. It is obvious, however, that with the exception of the reflections appearing in the plane containing the axis of rotation,

the modified reflections must move along the circles which are their loci in order that they may remain in the respective planes of incidence. To find their position rigorously, it would be necessary, at each setting of the crystal to find anew the planes of incidence and redraw the radial lines in the diagram the intersection of which with the circles of the powder-diagram gives the modified reflections. The trouble of doing this may, however, be avoided and the positions located with fair accuracy by a simple device, namely by finding the layer lines on which appear the Bragg reflections when the crystal is rotated or oscillated about the specified axis. It is evident that the points at which these layer lines intersect the powder-diagram circles represent the position of the modified reflections *rigorously* for the particular orientation of the crystal at which they coincide with the corresponding Bragg reflections, and therefore *approximately* also for a considerable range of orientations on either side of that position. In Fig. 3, the layer lines have been drawn for the case mentioned above, and the positions of the modified reflections marked therein. On comparing the same with Fig. 1, it will be seen that the displacements from their positions in the normal setting of the crystal are not large.

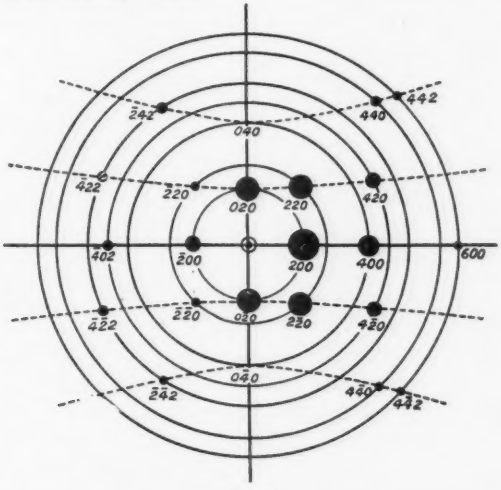

FIG. 3

Pattern of Modified Reflections with Crystal tilted about [010] Axis

4. *Experimental Results*

Plates V, VI and VII reproduce a series of 12 Laue photographs (Figs. 4 to 15) obtained with a crystal of rock-salt and the unfiltered radiation from a molybdenum target, the distance from crystal to photographic film being

4·9 cms. in the whole series. In obtaining Fig. 4, the crystal was set with the X-ray beam normal to a cube-face, in other words parallel to an axis of four-fold symmetry, and the pattern accordingly shows the same type of symmetry. In obtaining the remaining seven photographs of the series Figs. 5 to 11, the setting of the crystal was altered a few degrees at a time, being turned round a vertical axis of four-fold symmetry in the crystal. The patterns accordingly exhibit two-fold symmetry about a horizontal axis. The inclination of the X-ray beam to the four-fold axis of symmetry increased from 0° in Fig. 4 to 17° 46′ in Fig. 11. Figs. 12 to 15 in Plate VII reproduce another series of Laue photographs obtained by the same procedure but at larger angular intervals for the setting of the crystal and covering a greater range of incidences. To permit of this being done, the photographic film was displaced sideways so that it exhibits only one half of the Laue pattern. The inclination of the X-ray beam to the four-fold axis of symmetry was 0° in Fig. 12 and 25° 21′ in Fig. 15. Plate VIII reproduces two Laue photographs (Figs. 16 and 17) obtained with the unfiltered X-radiation from molybdenum and copper targets respectively, the rock-salt crystal being set so that the X-ray pencil was parallel to a diogonal axis of symmetry, in other words inclined at 45° to the cube faces.

A careful study of the Laue photographs reproduced in the plates brings out clearly the laws of the modified reflection of X-rays. The series of Figs. 4 to 15 in the plates should be compared with Fig. 1 and Fig. 3 in the text above in which the theoretical positions of the modified reflections have been indicated. Figs. 16 and 17 in the plate may also be compared with Fig. 2 in the text which refers to the same orientation of the crystal. It will be seen that there is a satisfactory agreement in each case between the theory and the experimental results. The most striking features brought out by the photographs are (1) the invariability of the angular separation between the incident beam and the modified reflections and (2) the remarkable resemblance between the pattern of modified reflections for an oblique setting of the crystal with the layer-line diagram of an oscillating or rotating crystal. This resemblance is clearly the consequence of the mechanism by which the modified reflections are brought into existence, namely the rotation of the dynamic stratifications of electron density with respect to the crystal spacings by the phase-waves of the lattice vibration. The rotation is of such magnitude that the angle $(\theta + \phi)$ between the incident pencil and the modified reflection by any particular plane remains invariant, though the crystal setting is altered. In other words, the modified reflection appears at the same angular separation from the primary beam as the Bragg reflection for a different setting of the crystal.

5. *Intensity Relations*

We shall now proceed to consider in detail the remarkable changes which occur in the *intensity* of the modified reflections as the setting of the crystal is altered. These form an impressive feature in the photographs.

The most intense reflections are those given by the (100) planes, as is to be expected. These are observed over a wide range of incidences in the second, fourth and sixth orders, but in decreasing order of intensity. The second order may be positive or negative, the reflection in the latter case appearing on the side of the plane opposite to that on which the X-ray beam is incident, which is rather a noteworthy phenomenon. Modified reflections of several different orders may be simultaneously observed, and in such cases, the relative intensity of the different orders depends on the setting of the crystal. For instance, in Figs. 14 and 15, the second, fourth and sixth order reflections by the (100) planes may all be observed, but the fourth order is the most intense in Fig. 14 and the sixth order in Fig. 15. The intensity of a reflection of any particular order is greatest when θ and ϕ are nearly equal, that is when the modified reflection appears in the vicinity of an ordinary or Bragg reflection of the same order from the planes under consideration. The intensity falls off when θ and ϕ diverge from each other in either direction. This fall is very rapid when θ is nearly equal to ϕ, as is evident from the photographs and strikingly illustrated by the fact (see for instance Fig. 9) that the $K\beta$ reflection may actually be stronger than the K_α reflection when it is nearer the Laue spot due to the same spacing. The fall of intensity however, becomes relatively slow when θ and ϕ differ greatly, and this fact enables the modified reflections to be observed over a wide range of incidences.

The (110) planes also give intense modified reflections, which may be observed in the second order, positive as well as negative and, though rather weakly, also in the fourth order (see Fig. 15). That these reflections are definitely weaker than the corresponding (100) reflections, may be seen for instance from Fig. 7, in which the second order (negative) reflections from the (110) planes have almost vanished, while those from the (100) are still quite strong. In some settings of the crystal, the (110) reflections may appear stronger than the corresponding (100) reflections, *e.g.*, in Figs. 14 and 15 where the 220 spots are stronger than the 200 spots, but this is merely due to the great disparity in the relative values of θ and ϕ for the two reflections.

Next in order of intensity are the 420 modified reflections, *i.e.*, those by the (210) planes in the second order. They may be seen above and below

the 400 modified reflections and on the same layer line as the 020 and 220 modified reflections (Figs. 10, 11, 13, 14 and 15) and may be readily compared in intensity with them. It will be noticed that the (420) spots though less intense than the 020 and 220 spots are comparable in intensity with the 400 spots and in some photographs actually brighter than them (see for instance Fig 15). These observations indicate that the modified reflections by the crystal planes appearing in the first column of Table I follow the same order of intensity as the unmodified reflections by those planes. The figures given in Table I further suggest that the 422 modified reflections should be weaker than the 420 and 400 modified reflections. That this is actually the case may be seen from Fig. 11 in which these reflections are seen in comparable circumstances (the 420 and 400 spots in the right half of the picture, and the 422 spots in the left half). See also Figs. 6, 8, 9 and 11. From Table I, we may also expect that the (221) planes should give modified reflections (in the second order) of comparable intensity with the fourth order reflections from the (110) planes and the sixth order reflections from the (100) planes. The 442 reflections may be seen clearly in Fig. 5 and their intensity is about the same as the 110 (4) and 100 (6) reflections seen in Fig. 15 in comparable circumstances.

6. *Verification of the Modified Bragg Formula*

In the theoretical paper by Raman and Nath quoted above, two alternative formulæ have been deduced, namely

$$2\,d \sin \tfrac{1}{2}(\theta + \phi) = n\,\lambda \qquad (1)$$

$$d \sin (\theta + \phi) = n\,\lambda \cos \phi \qquad (2)$$

which connect the glancing angles of incidence and reflection θ and ϕ respectively with the crystal spacing d, the order of reflection n and the X-ray wave-length λ. It was indicated that the considerations on which formula (1) was derived were probably valid for the great majority of crystals. In the preceding discussion, formula (1) has been assumed to be correct, but it is evidently of importance that the experimental data should be compared with both of the formulæ as a test of the theoretical considerations on which they were respectively based. The results given by the two formulæ differ to a greater extent the more widely θ and ϕ diverge from each other. The formulæ however become identical when $\theta = \phi$. Further, if the angles θ and ϕ are small,

$$2 \sin \tfrac{1}{2}(\theta + \phi) \backsimeq \sin (\theta + \phi) \text{ and } \cos \phi \backsimeq 1,$$

and hence in these circumstances the two formulæ cease to be experimentally indistinguishable. Accordingly for a discrimination between them to be

possible, it should be based on those cases when θ and ϕ differ considerably, and ϕ is as large as possible.

We give below in a series of Tables, the data measured from the photographs for the various orders of reflections by the spacings listed in the first column of Table I.

TABLE II

200 *Reflections*: *Crystal Spacing* = 2·814 *A.U.*

Crystal planes and Order of Reflection	X-Ray Wavelength A.U.	Glancing Angle of Incidence θ	Glancing Angle of Reflection ϕ	$\theta + \phi$	Spacing calculated from	
					Formula (1) A.U.	Formula (2) A.U.
+ 100 (2) ..	0·708	0°	14°19′	14°19′	2·84	2·77
		2°17′	11°55′	14°12′	2·86	2·82
		3°33′	10°46′	14°19′	2·84	2·81
		4° 4′	10°21′	14°25′	2·82	2·80
		9°40′	4°45′	14°25′	2·82	2·83
		11°36′	2°43′	14°19′	2·84	2·86
		14°47′	− 0°35′	14°12′	2·86	2·89
		17°46′	− 3°34′	14°12′	2·86	2·88
		25°21′	−11° 9′	14°12′	2·86	2·83
+ 100 (2) ..	0·625	0°	12°39′	12°39′	2·83	2·79
		4° 4′	8°35′	12°39′	2·83	2·82
		9°40′	2°46′	12°26′	2·89	2·90
		11°36′	1° 3′	12°39′	2·83	2·85
− 100 (2) ..	0·708	0°	−14°12′	−14′12°	2·86	2·80
		2°17′	−16°36′	−14′19°	2·84	2·74
		3°33′	−17°52′	−14°19′	2·84	2·72
		4° 4′	−18°16′	−14°12′	2·86	2·74
		9°40′	−23°59′	−14°19′	2·84	2·62

TABLE III

220 *Reflections*: *Crystal Spacing* = 1·990 *A.U.*

Crystal planes and Order of Reflection	X-Ray Wavelength A.U.	Glancing Angle of Incidence θ	Glancing Angle of Reflection ϕ	$\theta + \phi$	Spacing calculated from	
					Formula (1) A.U.	Formula (2) A.U.
+ (110) (2) ..	0·708	0°	20°10′	20°10′	2·02	1·93
		4°21′	15°55′	20°16′	2·01	1·97
		6°53′	13°31′	20°24′	2·00	1·98
		7°58′	12°26′	20°24′	2·00	1·98
		12°20′	7°50′	20°10′	2·02	2·03
+ (110) (2) ..	0·625	6°53′	10°53′	17°46′	2·02	2·01
		10°20′	7°32′	17°52°	2·01	2·02
		12°20′	5°20′	17°40′	2·04	2·05
− (110) (2) ..	0·708	0°	−20°10′	−20°10′	2·02	1·93
		1°39′	−21°49′	−20°10′	2·02	1·91
		1°51′	−22° 1′	−20°10′	2·02	1·90
		2°14′	−21°53′	−19°39′	2·07	1·95

TABLE IV

400 *Reflections*: *Crystal Spacing* = 2·814 *A.U.*

Crystal planes and Order of Reflection	X-Ray Wavelength A.U.	Glancing Angle of Incidence θ	Glancing Angle of Reflection ϕ	$\theta + \phi$	Spacing calculated from	
					Formula (1) A.U.	Formula (2) A.U.
(100) (4) ..	0·708	9°40′	19°18′	28°58′	2·83	2·76
		11°36′	17°26′	29° 2′	2·82	2·78
		17°46′	11°22′	29° 8′	2·82	2·85
		19°21′	9°57′	29°18′	2·80	2·85
		25°21′	3°57′	29°18′	2·80	2·89
(100) (4) ..	0·625	9°40′	15°58′	25°38′	2·82	2·78
		11°36′	14° 8′	25°44′	2·81	2·79
		14°47′	10°57′	25°44′	2·81	2·83
		17°46′	7°58′	25°44′	2·81	2·85

TABLE V

240 *and* 420 *Reflections*: *Crystal Spacing* = 1·259 *A.U.*

Crystal planes and Order of Reflection	X-Ray Wavelength A.U.	Glancing Angle of Incidence θ	Glancing Angle of Reflection ϕ	$\theta + \phi$	Spacing calculated from	
					Formula (1) A.U.	Formula (2) A.U.
(120) (2) and (210) (2)	0·708	13° 3′	19°27′	32°30′	1·27	1·24
		13°17′	19°13′	32°30′	1·27	1·24
		14°53	17°37′	32°30′	1·27	1·26
		15°24′	17°14′	32°38′	1·26	1·25
		15°32′	17° 2′	32°34′	1·26	1·26
		16°59′	15°35′	32°34′	1·26	1·27
	0·625	13° 3′	15°27′	28°30′	1·27	1·26
		13°17′	15°19′	28°36′	1·27	1·26
		14°53′	13°59′	28°52′	1·25	1·26
		15°24′	13°20′	28°44′	1·26	1·26
		15°32′	12°58°	28°30′	1·27	1·28
		16°59′	11°53′	28°52′	1·25	1·27

TABLE VI

242 *and* 422 *Reflections*: *Crystal Spacing* = 1·149 *A.U.*

Crystal planes and Order of Reflection	X-Ray Wavelength A.U.	Glancing Angle of Incidence θ	Glancing Angle of Reflection ϕ	$\theta + \phi$	Spacings calculated from	
					Formula (1) A.U.	Formula (2) A.U.
(121) (2) and (211) (2)	0·708	15° 6′	20°36′	35°42′	1·15	1·13
		15°32′	20°20′	35°52′	1·15	1·13
		16°29′	19°27′	35°56′	1·15	1·14
		16°59′	18°57′	35°56′	1·15	1·14
		18°32′	17°24′	35°56′	1·15	1·15
		20°29′	15°27′	35°56′	1·15	1·16
		20°35′	15°21′	35°56′	1·15	1·16
	0·625	15° 6′	16°24′	31°30′	1·15	1·15
		15°32′	16° 4′	31°36′	1·15	1·15
		16°29′	16°11′	31°40′	1·15	1·14
		16°59′	14°53′	31°52′	1·14	1·15
		18°32′	13° 8′	31°40′	1·15	1·16

TABLE VII

440 *Reflections*: *Crystal Spacing* = 1·990 *A.U.*

Crystal planes and Order of Reflection	X-Ray Wavelength A.U.	Glancing Angle of Incidence θ	Glancing Angle of Reflection ϕ	$\theta + \phi$	Spacing calculated from	
					Formula (1) A.U.	Formula (2) A.U.
(110) (4) ..	0·708	17°29′	24°19′	41°48′	1·99	1·94
	0·625	17°29′	18°49′	36°18′	2·01	2·00

TABLE VIII

442 *Reflections*: *Crystal Spacing* = 0·938 *A.U.*

Crystal planes and Order of Reflection	X-Ray Wavelength A.U.	Glancing Angle of Incidence θ	Glancing Angle of Reflection ϕ	$\theta + \phi$	Spacing calculated from	
					Formula (1) A.U.	Formula (2) A.U.
(221) (2) ..	0·708	20°48′	23°36′	44°24′	0·937	0·927
		21°27′	22°47′	44°14′	0·940	0·935

TABLE IX

600 *Reflections*: *Crystal Spacing* = 2·814 *A.U.*

Crystal planes and Order of Reflection	X-Ray Wavelength A.U.	Glancing Angle of Incidence θ	Glancing Angle of Reflection ϕ	$\theta + \phi$	Spacing calculated from	
					Formula (1) A.U.	Formula (2) A.U.
(100) (6)	0·708	19°21′	24°45′	44°6′	2·83	2·74
		25°21′	19° 3′	44°24′	2·81	2·87

The figures appearing in the last two columns of Tables II, III, IV, V, VI, VII, VIII and IX all show in an unmistakable manner that the symmetric formula (1) and *not* the asymmetric formula (2) gives results in agreement with experiment in the case of rock-salt. The differences between the actual crystal spacings and those calculated from the asymmetric formula are systematic and in the expected direction: they increase when θ and ϕ diverge from each other, being positive when θ is greater than ϕ and negative when θ is less than ϕ. The differences become great when ϕ is numerically large, just as we should expect. The errors in measurements of the angles of θ

and ϕ are relatively the greatest in the case of the 200 reflections, both because the absolute values of θ and ϕ are then smallest, and also because the spots being intense, are heavily overexposed and therefore subject to photographic broadening. It is therefore not surprising that the agreement between the actual crystal spacings and those calculated from the symmetric formula and shown in the penultimate column of Table II is not as excellent as it is in the case of the reflections listed in Tables III to IX. Even so, the failure of the asymmetric formula for the 200 reflections is as evident as in the other cases.

7. *Significance of the Results*

The asymmetric formula (2) referred to above may be written in the form

$$d(\sin\theta + \cos\theta \tan\phi) = n\lambda \qquad (2')$$

A formula of identically the same form as (2′) appears as equation (12) of a theoretical paper by Faxen (1923) *in which ϕ now denotes the direction of maximum intensity in the diffuse thermal scattering of monochromatic X-rays by a cubic crystal.* Faxen's theory has been recently revived and developed by Zachariasen (1940) in an attempt to explain the radial streaks in Laue patterns observed by many workers as well as the more recent experimental results obtained in this connection by Wadlund (1938), Preston (1939) and of Siegel and Zachariasen (1940). As we have seen above, the formula (2′) fails to represent the actual position of the modified reflections observed with rock-salt when the incidences are varied over a sufficient range of angles to make a real test of its validity. The experimental results thus clearly indicate that the Faxen-Zachariasen theory is inadequate to explain the phenomena under consideration in the present series of papers. Further, the success of the modified Bragg formula (1) in giving correctly the position of the spots as observed in the present investigation over a wide range of incidences indicates clearly that we are dealing here with a distinctive phenomenon which is in the nature of a specular reflection of the X-rays, and not a diffuse scattering.

It will be noticed that the modified reflections given by rock-salt are much better defined than those obtained with sodium nitrate, expecially when the angles of incidence and reflections differ greatly. This is not surprising when it is remembered that the melting point of rock-salt is 804° C. as against 308° C. for sodium nitrate, and that the characteristic frequencies of the latter substance (at any rate some of them) are much lower than that of rock-salt. The disturbing effect of thermal agitation on the modified reflections should therefore be much more serious with sodium nitrate than

with rock-salt. The theoretical derivation of the symmetric formula makes it clear that the reflections given by that formula should appear in sharply defined directions, and any lack of definition must therefore be due to disturbing causes such as thermal agitation or the mosaic structure of the crystal. The question here raised can be resolved by experiments with the substance at low temperatures. Such experiments have been taken in hand.

8. *Summary*

The paper presents an experimental study and theoretical discussion of the modified reflection of X-rays in rock-salt. It is shown that the oscillation of the interpenetrating lattices of sodium and chlorine ions would vary the structure amplitudes of the crystal in such a way that the halved spacings which give strong unmodified reflections would also give strong modified reflections in the same order of relative intensity. This is supported by the experimental results. A geometrical construction is given for deriving the modified reflection patterns in various cases and it is shown that for an oblique setting of the crystal, there is a remarkable similarity between the patterns and the layer-line diagram of the Bragg reflections by an oscillating crystal. The modified Bragg law $2\,d \sin \frac{1}{2}(\theta + \phi) = n\,\lambda$ is in very satisfactory agreement with the experimental results.

REFERENCES

Raman and Nilakantan	..	*Proc. Ind. Acad. Sci.*, 1940, **11**, 389, 398.
————and Nagendra Nath		*Ibid.*, 1940, **12**, 83.
Bragg, James and Bosanquet	..	*Phil. Mag.*, 1921, **41**, 309.
Barnes ..	..	*Zt. f. Phys.*, 1932, **75**, 723.
Fermi and Rasetti ..	..	*Ibid.*, 1931, **71**, 689.
Faxen ..	..	*Ibid.*, 1923, **17**, 266.
Zachariasen ..	..	*Phys. Rev.*, 1940, **57**, 597.
Wadlund ..	..	*Ibid.*, 1938, **53**, 843.
Preston ..	..	*Proc. Roy. Soc.*, A, 1939, **172**, 116.
Siegel and Zachariasen	..	*Phys. Rev.*, 1940, **57**, 795.

FIG. 4

FIG. 5

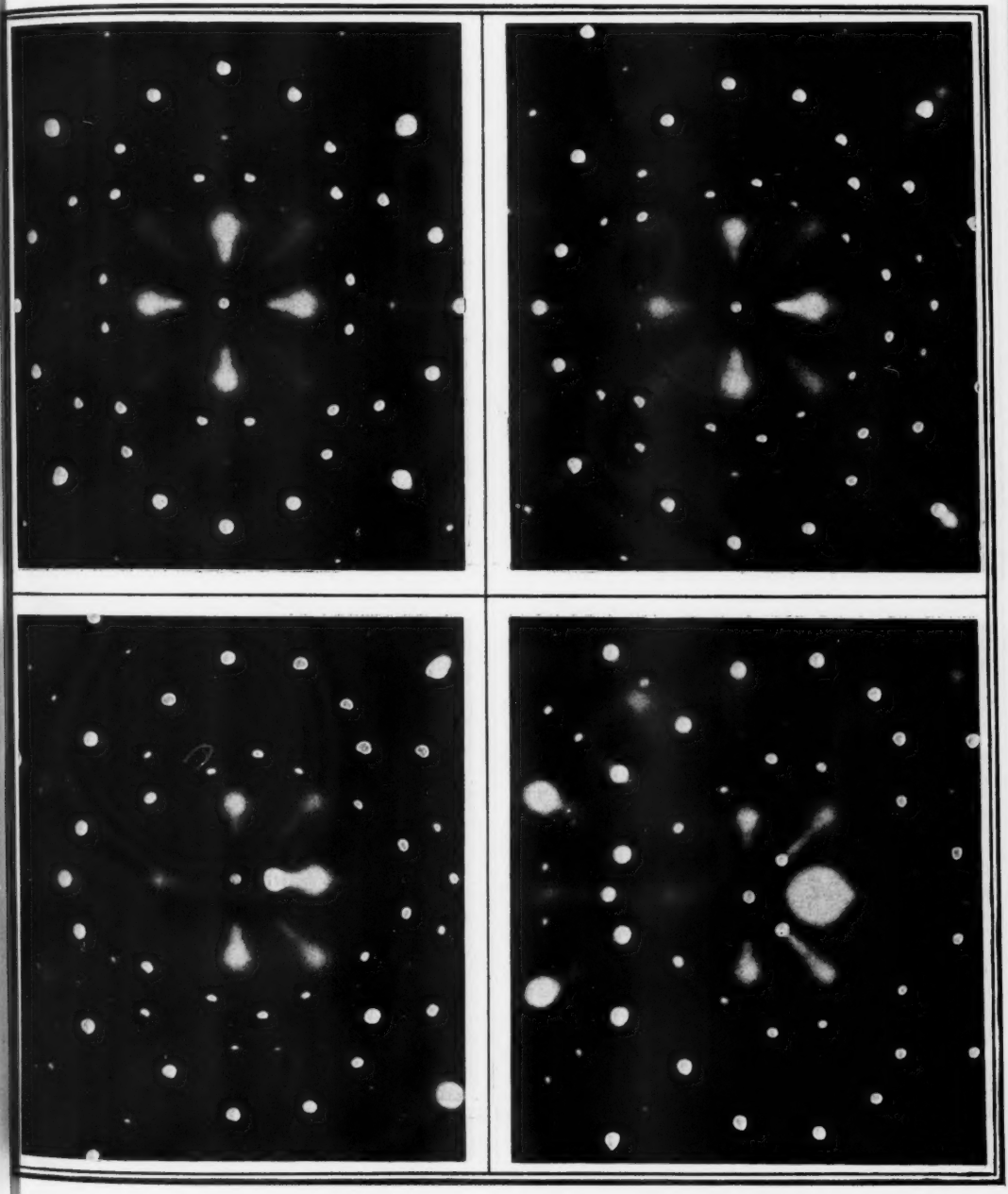

FIG. 6

FIG. 7

Laue Photographs with Rock Salt showing Modified Reflections

FIG. 8

FIG. 9

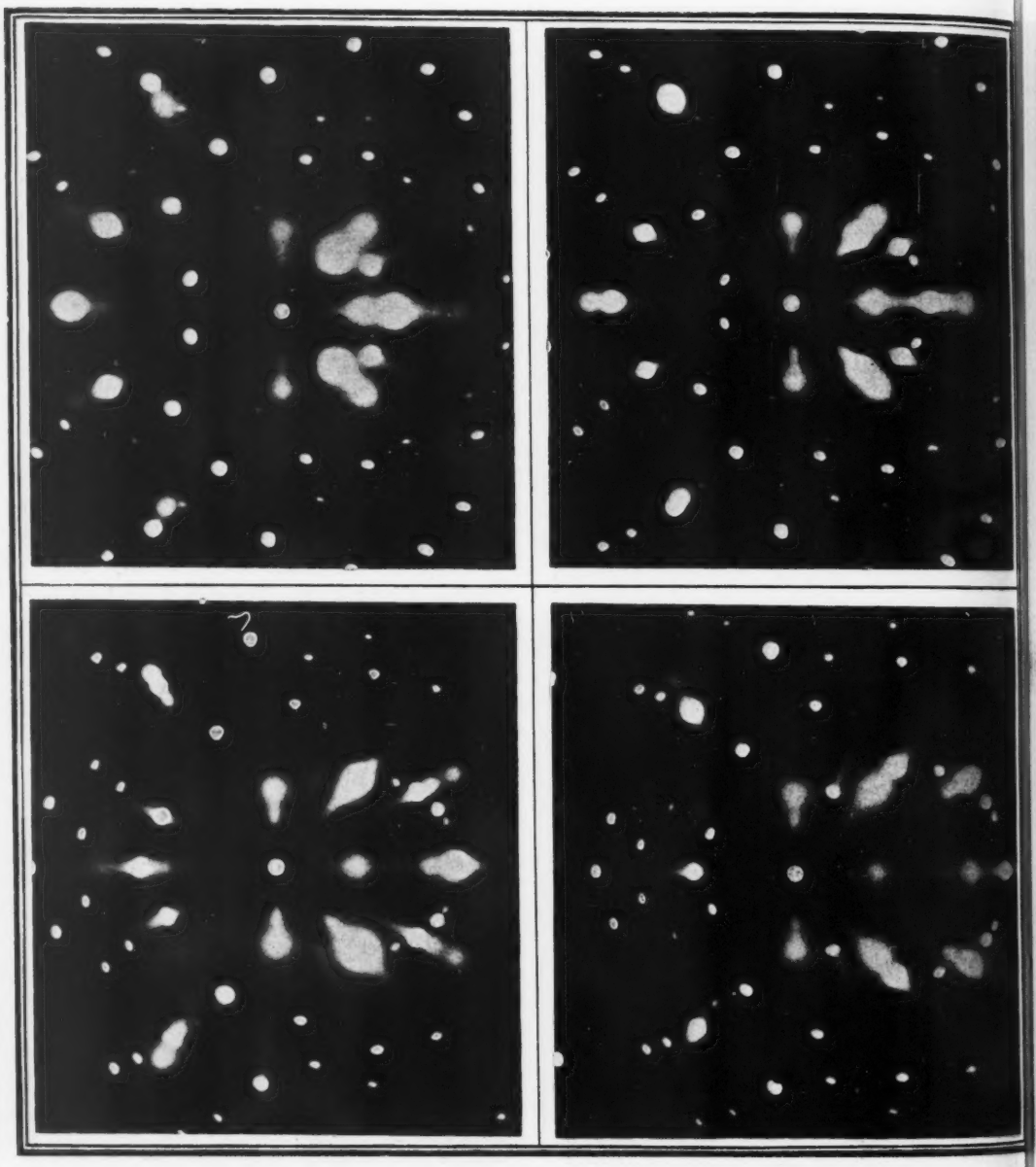

FIG. 10

FIG. 11

Laue Photographs with Rock Salt showing Modified Reflections

FIG. 12

FIG. 13

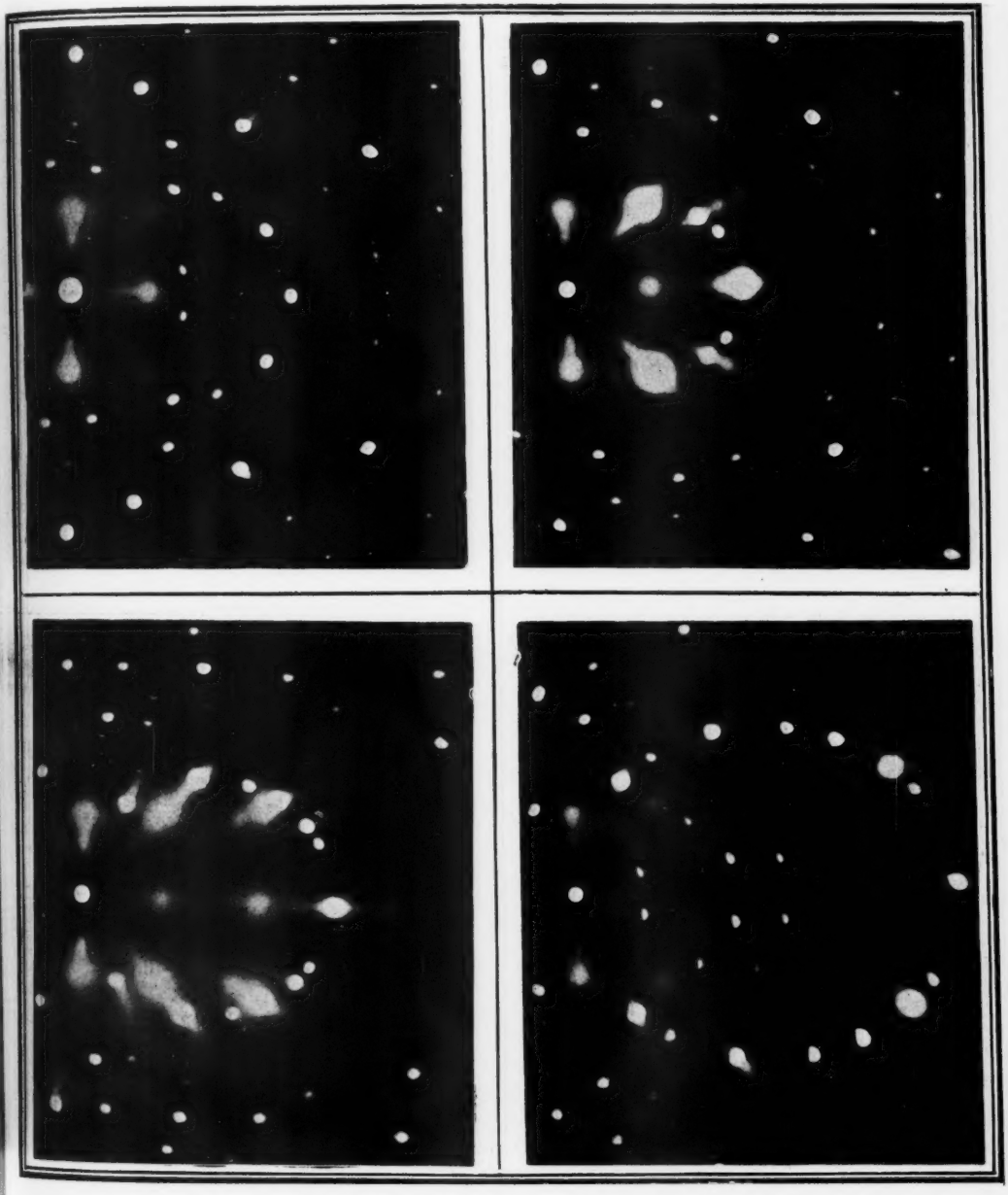

FIG. 14

FIG. 15

Laue Photographs with Rock Salt showing Modified Reflections

FIG. 16

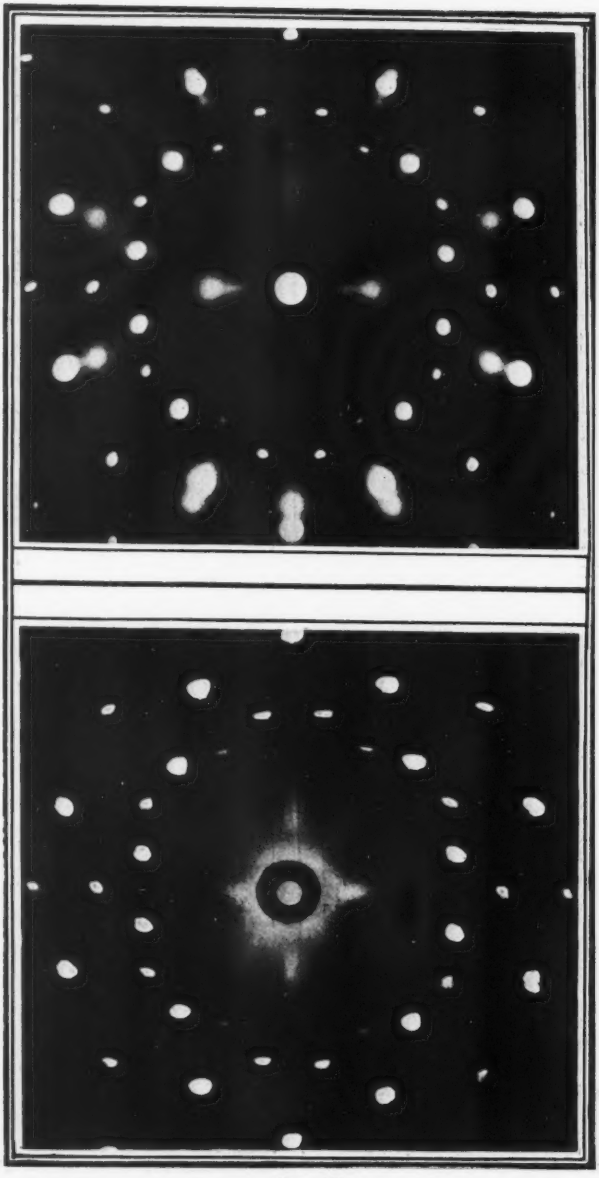

FIG. 17

Laue Photographs with Rock Salt showing Modified Reflections

STUDIES ON THE DEPENDENCE OF OPTICAL ROTATORY POWER ON CHEMICAL CONSTITUTION

Part XVIII. The Rotatory Dispersion of Stereo-isomeric 3.nitro-*o*-toluidino-, 5.nitro-*o*-toluidino-, 2:3-toluylenebisamino- and 2:5-toluylenebisamino- methylenecamphors

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Received June 26, 1940

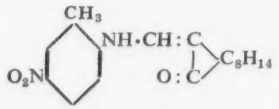
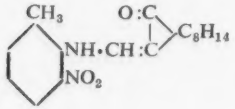
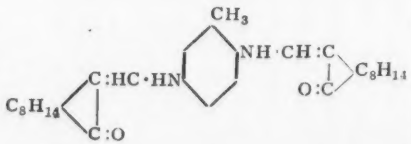
IN this communication we present further new experimental data on the rotatory dispersion of the condensation products of oxymethylenecamphors (*d*, *l* and *dl*) with aromatic nitramines and the corresponding diamines, namely, 3·nitro-*o*-toluidine, 5·nitro-*o*-toluidine, 2:3-toluylenediamine and 2:5-toluylenediamine.

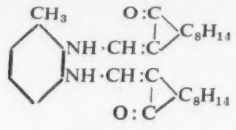
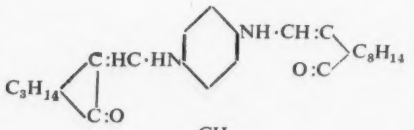
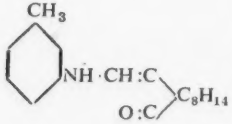
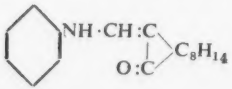
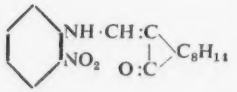
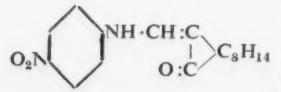
The Influence of Chemical Constitution on Rotatory Power.—Rotatory dispersions are classified as "Simple" or "Complex" according as they can, or cannot, be expressed by Drude's one-term equation, $[\alpha] = \frac{k}{\lambda^2 - \lambda^2_0}$. Oxymethylenecamphors and their condensation products with aromatic mono- and di-amines[1] were found to obey the simple dispersion formula exactly. From the present investigation, it appears that the rotatory dispersions of the above-mentioned condensation products can also be expressed by the one-term expression of Drude's equation (Tables I–XXIII). On plotting $1/[\alpha]$ against λ^2, exact straight lines were obtained which are not reproduced. The specific rotations observed and calculated from the dispersion formulæ agree well within the limits of experimental error. The wide range of applicability of the simple dispersion formula to varied types of organic compounds in solution is thus further established. The nature of the solvent has absolutely no effect whatever on the type of rotatory dispersion in this series of compounds, as can be seen from the measurements given in Tables I–XXIII.

Effect of Substituents on Rotatory Power.—The effect of the nitro group on the rotatory power in these compounds has been investigated.

[1] Singh and Bhaduri, *J. Ind. Chem. Soc.*, 1930, **7**, 771; 1931, **8**, 181; Singh, Bhaduri and Barat, *ibid.*, 1931, **8**, 345.

TABLE A

Structural Formulæ	Order of rotatory power	$[\alpha]^{35°C}_{Hg_{5461}}$					
		Solvent					
		1	2	3	4	5	6
		Pyridine	Chloroform	Acetone	Ethyl alcohol	Methyl alcohol	Benzene
		Dielectric constants					
		12·4	5·2	21·5	25·8	31·2	2·28
I 	1 > 2 > 3 > 4 > 5 > 6	561·5	523·3	522·1	500·7	491·8	479·4
II 	1 > 3 > 5 > 4 > 6	270·8*	..	234·8*	229·7*	232·4*	190·6
III 	1 > 2 > 4 > 3 > 5 > 6	761·8	739·5	700	725·5	694·9	661

A2a	IV		1 > 2 > 3 > 5 > 4 > 6	466·9	427·8	420	363·2	415·4	323·7
	† V			712·5	689·2	..	..	..	..
	‡ VI			405·8	384·8	442·3	439·9	454·4	352·6
	§ VII			433·2	424·6	448·9	451·3	480·0	367·1
	§ VIII			424·8	484·6	468·1	..	493·1	399·2
	§ IX			545·0	493·5	519·4	..	510·7	437·0

* Calculated values.

† Singh and Bhaduri, *J.I.C.S.*, 1930, **7**, 771.

‡ Singh, Bhaduri and Barat, *ibid.*, 1931, **8**, 345.

§ Singh and Barat, *J.I.C.S.*, 1940, **17**, 1.

The general effect of the nitro group seems to be to increase the rotatory power of the parent substance. Thus the rotatory power of nitroanilinomethylenecamphors is greater than that of the parent compound, *i.e.*, anilinomethylenecamphor (Table A). Further the nitro group in the para-position to the substituted amino group increases the rotation to a greater extent than when it is in the ortho position (Table A, VII, VIII, IX). The position of the nitro group in the present series of compounds has also a similar influence on the rotatory power. Thus when the nitro group is in the 5-position, *i.e.*, para-position to the substituted amino group, the specific rotatory power is much higher than when it is in the 3-position, *i.e.*, ortho-position to the substituted amino group (Table A, I and II). Since the parent compound, *o*-toluidinomethylenecamphor, is not known, the effect of the nitro group cannot be studied in the case of its nitro derivatives, *i.e.*, it cannot be compared with I and II.

The introduction of additional optically active centres in nitro-*o*-toluidinomethylenecamphors (Table A, I and II) does not result in corresponding increase of the values of rotatory power. This is clear from a comparison of the rotatory powers of 5·nitro-*o*-toluidinomethylenecamphor (I) with 2:5-toluylenebisamino-methylenecamphor (III) and that of 3·nitro-*o*-toluidino-methylenecamphor (II) with 2:3-toluylenebisaminomethylenecamphor (IV): the rotations of the bisaminomethylenecamphor compounds (III and IV) are less than twice the values for the corresponding mono-aminomethylenecamphor derivatives (I and II). These results are further supported from the rotatory power data of *m*-toluidino-methylenecamphor (VI) and 2:5-toluylenebisaminomethylenecamphor (III). The introduction of additional optically active centres may even result in the decrease of rotatory power; thus the rotatory power of 2:3-toluylenebisaminomethylenecamphor (IV) is less than that of *m*-toluidinomethylenecamphor (VI) in four solvents, namely, acetone, ethyl and methylalcohols and benzene, although it is greater in pyridine and chloroform. The above-mentioned facts can only be explained by supposing that ortho-substitution results in a decrease of the rotatory power, while para-substitution causes an increase.

The influence of the CH_3 group on the rotatory power does not follow any rule. Sometimes it causes an increase in the rotatory power and at other times a decrease. Thus the rotatory power of 2:5-toluylenebisamino-methylenecamphor (III) is higher than that of *p*-phenylonebisaminomethylenecamphor (V). Similarly the rotatory power of 5·nitro-*o*-toluidinomethylenecamphor (I) is higher than that of *p*-nitroanilinomethylenecamphor (IX). But the rotatory power of 3·nitro-*o*-toluidinomethylenecamphor (II) is much less than that of *o*-nitroanilinomethylenecamphor (VIII).

The Influence of Solvent on Rotatory Power.—The specific rotatory power of the four compounds (I–IV) for Hg_{5461} in the six solvents has been given in Table A. It is found that the order of decreasing rotatory power is : Pyridine> chloroform> acetone> ethyl alcohol> methyl alcohol> benzene in the case of 5·nitro-*o*-toluidinomethylenecamphor (I); in the cases of 3·nitro-*o*-toluidinomethylenecamphor (II) and 2 : 3-toluylenebisaminomethylenecamphor (IV), the order for ethyl alcohol and methyl alcohol has been reversed; and in the case of 2 : 5-toluylenebisaminomethylenecamphor (III), that for acetone and ethyl alcohol. It is thus clear that the order of the rotatory power in different solvents does not run parallel with the sequence of their dielectric constants, namely, methyl alcohol> ethyl alcohol> acetone> pyridine> chloroform> benzene.

The Physical Identity of Enantiomers.—According to Pasteur's principle of molecular dissymmetry, the *d*- and *l*-forms of a compound are represented as mirror images of one another, differing in sign, but absolutely identical in the numerical value of their rotatory power. They must have similar mechanical stability and therefore have an equal chance of formation. They must also have the same scaler properties. But they should differ in those physical properties which are of the directional (vectorial) nature, such as, for example, direction of rotation of the plane of polarised light. On the other hand, according to wave-mechanics[2] the *dextro* and *lævo* forms of a compound, however, differ slightly in their rotatory powers, but this is not supported by these observations (Tables I–XXIII). Pasteur's law thus stands confirmed.

The individual readings of the angle of rotation did not differ from the mean by more than 0·02°. A calculation from the tables of rotatory dispersion will show that the maximum errors obtained by working out the effects on the result of the maximum deviation (0·02°) are well within the limits of attainable experimental accuracy. Only in ten cases out of 376 observations now recorded, we find that the deviation is about 0·03°. These are, however, casual experimental errors.

The melting points of the racemic forms of 5-nitro-*o*-toluidinomethylenecamphor and 3·nitro-*o*-toluidinomethylenecamphor are higher than those of their optically active isomers. These forms are true *dl*-compounds, at least in the solid state.

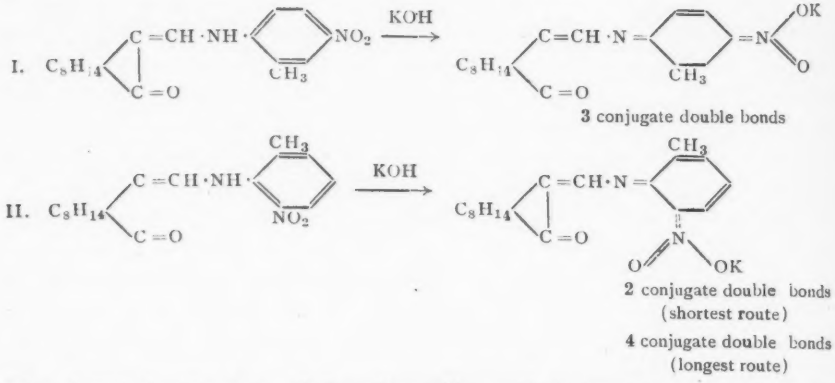
The effect of the position of the nitro group on the colour of the dyes.—5·nitro-*o*-toluidinomethylenecamphors and 3·nitro-*o*-toluidinomethylene-

[2] Temple, *Trans. Faraday Soc.*, 1930, **26**, 272.

camphors are dye-stuffs. The depth of colour in these dye-stuffs depends on the position of the nitro group: when the nitro group is in the para-position to the substituted amino group (I, Table A), the colour of the dye-stuff is bright yellow, but when the nitro group is in the ortho-position (II, Table A), the colour is deep orange. In alcoholic potassium hydroxide solutions the colour of 5·nitro-*o*-toluidinomethylenecamphor is deep violet and that of the 3·nitro-*o*-toluidinomethylenecamphor is port wine red (Table B).

Similarly, *p*-nitroanilinomethylenecamphor is bright yellow in the solid state, whereas the *o*-nitroanilinomethylenecamphor is orange red. In alcoholic alkaline solutions the former gives a deep violet colour and the latter an orange yellow colour (Table B). These colour reactions are thus similar to those found in the cases of the nitro-*o*-toluidinomethylenecamphors.

The above-mentioned remarkable changes in colour in alkaline solutions of these compounds must be correlated with changes in their structures as indicated below:



The change in structure of the nitroanilinomethylenecamphors in alcoholic alkaline solutions can be represented similarly as above.

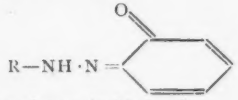
The nitro group in the presence of alkalis changes into the *isonitro-* or *aci-* modification which enables it to form salts with alkali, producing thereby quinonoid structures.

Various explanations have been put forward to account for the depth of colour: Hewitt[3] enunciated that the colour is deeper the longer the conjugate chain in the molecule. Watson[4] suggested that Hewitt's rule should be

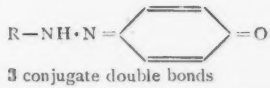
[3] *J.C.S.*, 1907, **91**, 1251.

[4] *Ibid.*, 1914, **105**, 764.

modified so that the conjugate chain is contained in a quinonoid formula of the substance. Sircar[5] further modified Hewitt's rule for the azo series, to the effect that the depth of colour was proportional to the length of the conjugate chain in the part of the molecule containing the auxochrome, proceeding from the auxochrome to the azo linking, taking the longest possible route. He further argued that deeper colours are obtained when the auxochromic and chromophoric groups are in the ortho-position and comparatively lighter colours when in the para-position with respect to each other, because in the former case there is a comparatively longer chain of alternate double and single bonds counting from the auxochrome to the chromophore, thus:



4 conjugate double bonds



3 conjugate double bonds

The results obtained by us are in general accord with the hypotheses of Hewitt, Watson and Sircar, but they are at variance with Sircar's view postulating the assumption regarding the route to be followed in counting the conjugate linkings. On Sircar's view the ortho compounds should have deeper colours than their para-isomerides, both in the cases of nitroanilinomethylenecamphors and nitro-*o*-toluidinomethylenecamphors in alkaline solutions, whereas opposite is the case as pointed out above (*vide* Table B). The colour of these substances in alcoholic solutions are also given in Table B for the sake of comparison:

TABLE B

Substance	Colour in solid state	Colour in ethyl alcohol	Colour in alkaline solution
5-nitro-*o*-toluidinomethylenecamphors (I, Table A)	bright yellow	yellow	deep violet
3-nitro-*o*-toluidinomethylenecamphors (II, Table A)	orange red	orange red	port wine red
o-nitroanilinomethylenecamphors (VIII, Table A)	orange red	orange red	orange yellow
p-nitroanilinomethylenecamphors (IX, Table A)	bright yellow	yellow	deep violet
**m*-nitroanilinomethylenecamphors ..	bright yellow	yellow	brownish yellow

* Singh and Barat, *J.I.C.S.*, 1940, **17**, 401.

[5] *J.C.S.*, 1916, **109**, 757.

m-nitroanilinomethylenecamphor which is yellow both in the solid state and in ethyl alcohol solution gives only a brownish yellow colour in alkaline solution. As there is no possibility of a tautomeric change leading to the production of a quinonoid structure in this compound, there is no change in the depth of colour on the additon of alkali.

The alkaline solutions of these dyestuffs, on acidification with dilute hydrochloric acid, gave the original substances.

Dyeing properties of 5·*nitro- and* 3·*nitro*-o-*toluidinomethylenecamphors.*— Both these substances have been tried as dyes on wool. Since the nitro dyes are applied with a mordant, two kinds of mordants have been used. They are (i) potassium acid sulphate and (ii) sodium sulphate (20%) with 3% sulphuric acid.

With the first mordant, 3·nitro-*o*-toluidinomethylenecamphor dyed wool a light yellow colour. Washing with soap had no effect on the colour but sunlight seemed to affect it after sometime. With the second mordant, it dyed wool a yellow colour and though it was fast to soap it was also affected similarly by sunlight.

5·nitro-*o*-toluidinomethylenecamphor developed a light yellow colour on wool with potassium acid sulphate as mordant. The colour was fast to soap but seemed to be somewhat affected by light after a long time. With sodium sulphate and sulphuric acid as mordant a very fine light yellow colour was produced on the wool which was unaffected by washings with soap. Sunlight, however, slightly affects it after a long time.

Experimental

The lævo- and racemic-isomers, which are described in this paper, were prepared by the same method as the corresponding dextro-compounds, and had similar crystalline form, colour and solubility. These compounds have characteristic odours, which will be discussed in a separate communication.

5·nitro-*o*-toluidine and 3·nitro-*o*-toluidine were prepared by slowly adding *o*-acetotoluidide (45 g.) to an ice-cold mixture of concentrated nitric acid (100 c.c.) and glacial acetic acid (50 c.c.) with constant stirring; the clear liquid after standing for 24 hours was poured into cold water and filtered. The solid substance thus obtained was subjected to steam distillation in the presence of strong hydrochloric acid (150 c.c.). The 3-nitro-*o*-toluidine distilled over as orange coloured needles, m.p. 94° C., while the 5·nitro-*o*-toluidine remained in the flask and was crystallised from dilute alcohol as yellow prisms, m.p. 130° C.

2:5-diaminotoluene dihydrochloride and 2:3-diaminotoluene dihydrochloride were prepared from the corresponding nitrotoluidines described above, by the method of Beilstein and Kuhlberg[6], with some modifications. The solution containing the product of reduction, stannic chloride and hydrochloric acid was evaporated to dryness to drive off the excess of the acid and digested with sufficient amount of water; the tin was completely precipitated as sulphide and filtered off. On evaporating, the base crystallised out as dihydrochloride. The 2:5-diaminotoluene dihydrochloride is obtained as white plates whereas the 2:3-isomer in light red plates. The dihydrochlorides char on heating without melting. They are freely soluble in water.

5·nitro-*o*-toluidinomethylene-*d*-camphor was prepared by mixing molecular proportions of oxymethylene-*d*-camphor (in 90% ethyl alcohol) and 5·nitro-*o*-toluidine (in 70% acetic acid). On keeping the mixture in ice for half an hour, the product of condensation was deposited as bright yellow needles. It was filtered and washed with dilute acetic acid and then with distilled water; m.p. 161–62°, yield 70%. (Found: N, 8·82 per cent.; $C_{18}H_{22}N_2O_3$ requires N, 8·91 per cent.) It is fairly soluble in most organic solvents, being very soluble in benzene, acetone, chloroform, pyridine and glacial acetic acid, less so in ethyl alcohol, moderately soluble in ether and insoluble in water.

5·nitro-*o*-toluidinomethylene-*l*-camphor, m.p. 162°. (Found: N, 8·83 per cent.; $C_{18}H_{22}N_2O_3$ requires N, 8·91 per cent.) 5. nitro-*o*-toluidinomethylene-*dl*-camphor, m.p. 170°. (Found: N, 8·98 per cent.; $C_{18}H_{22}N_2O_3$ requires N, 8·91 per cent.)

3·nitro-*o*-toluidinomethylene-*d*-camphor was prepared by mixing molecular proportions of oxymethylene-*d*-camphor (in 90% ethyl alcohol) and 3·nitro-*o*-toluidine (in glacial acetic acid). No crystals separated in this case, but on pouring the solution into water, deep red oil separated. The oil was allowed to stand under water for some days when it solidified. It was crystallised from dilute alcohol or ligroin, as orange red plates, m.p. 98°, yield 55%. (Found: N, 9·2 per cent.; $C_{18}H_{22}N_2O_3$ requires N, 8·91 per cent.) It is very soluble in benzene, ether and acetone, less so in ethyl alcohol, still less in ligroin and insoluble in water.

3·nitro-*o*-toluidinomethylene-*l*-camphor, m.p. 98°. (Found: N, 9·15 per cent.; $C_{18}H_{22}N_2O_3$ requires N, 8·91 per cent.) 3·nitro-*o*-toluidinomethylene-*dl*-camphor, m.p. 122° C. (Found: N, 8·87 per cent.; $C_{18}H_{22}N_2O_3$ requires N, 8·91 per cent.)

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[6] *Ann.*, 1871, **158**, 352.

2: 5-toluylenebisaminomethylene-*d*-camphor was prepared by adding two molecular proportions of oxymethylene-*d*-camphor (in 90% ethyl alcohol) to one molecular proportion of 2: 5-diaminotoluene dihydrochloride (in 30% acetic acid with a little sodium acetate). On mixing a yellow solid separated which was filtered and washed with water, and crystallised from dilute alcohol as yellow needles, m.p. 215° C., yield 70%. It was soluble in benzene, acetone, pyridine and ether, sparingly so in ethyl alcohol and methyl alcohol and insoluble in water. (Found: N, 6·2 per cent.; $C_{29}H_{38}N_2O_2$ requires N, 6·28 per cent.)

2: 5-toluylenebisaminomethylene-*l*-camphor, m.p. 217° C. (Found: N, 6·35 per cent.; $C_{29}H_{38}N_2O_2$ requires N, 6·28 per cent.) 2: 5-toluylenebisaminomethylene-*dl*-camphor, m.p. 136° C. (Found: N, 6·38 per cent.; $C_{29}H_{38}N_2O_2$ requires N, 6·28 per cent.)

2: 3-toluylenebisaminomethylene-*d*-camphor was prepared by treating two molecular proportions of oxymethylene-*d*-camphor (in 90% ethyl alcohol) with one molecular proportion of 2: 3-diaminotoluene dihydrochloride (in 30% acetic acid with sodium acetate). On mixing and rubbing a light orange coloured semi-solid was obtained. This was kept under water for a few days when it solidified. The solid was filtered and washed with water. On trying to crystallise it from chloroform, benzene or alcohol, it was again transformed into an oil. Hence it was purified by fractional precipitation from alcoholic solutions by the addition of water. The substance had a light yellow colour, m.p. 115° C., yield 60%. (Found: N, 6·40 per cent.; $C_{29}H_{38}N_2O_2$ requires N, 6·28 per cent.) It is very soluble in ether and toluene, moderately so in alcohol, benzene, pyridine and acetone, sparingly soluble in ligroin and insoluble in water.

2: 3-toluylenebisaminomethylene-*l*-camphor, m.p. 116° C. (Found: N, 6·37 per cent.; $C_{29}H_{38}N_2O_2$ requires N, 6·28 per cent.) 2: 3-toluylenebisaminomethylene-*dl*-camphor, m.p. 116° C. (Found: N, 6·38 per cent.; $C_{29}H_{38}N_2O_2$ requires N, 6·28 per cent.)

The rotatory power determinations were carried out in a 2-*d*. cm. jacketted tube at 35° C. The value of λ_0 calculated from the dispersion formula is given in the Tables and is expressed as μ or 10^{-4} cm.

TABLE I

5·nitro-o-toluidinomethylenecamphor in Methyl Alcohol

$$[\alpha] = \pm \frac{70{\cdot}4}{\lambda^2 - 0{\cdot}1555};\ \lambda_0 = 0{\cdot}3943$$

Dextro			Line λ	Calc. $[\alpha]$ $= c$	*Lævo*		
Concentration g./100 c.c.	Obs. $[\alpha]$ $= o$	$o-c$			$o'-c$	Obs. $[\alpha]$ $= o'$	Concentration g./100 c.c.
0·4544 g.	606·8°	+ 3·8°	Cu_{5218}	±603°	+ 0·2°	603·2°	0·4208 g.
	491·8	− 1·8	Hg_{5460}	493·6	− 2·9	490·7	
	385·1	+ 0·6	Hg_{5790}	384·5	+ 0·9	385·4	
	364·2	− 3·0	Na_{5812}	367·2	− 0·1	367·1	
	324·6	+ 0·2	Li_{6103}	324·4	− 0·8	323·6	
	282·8	+ 0·3	Zn_{6362}	282·5	± 0	282·5	
	268·5	+ 1·7	Cd_{6438}	266·8	− 1·7	265·1	
	238·7	− 0·7	Li_{6707}	239·4	− 2·1	237·3	

TABLE II

5·nitro-o-toluidinomethylenecamphor in Acetone

$$[\alpha] = \pm \frac{70{\cdot}01}{\lambda^2 - 0{\cdot}162};\ \lambda_0 = 0{\cdot}4025$$

Dextro			Line λ	Calc. $[\alpha]$ $= c$	*Lævo*		
Concentration g./100 c.c.	Obs. $[\alpha]$ $= o$	$o-c$			$o'-c$	Obs. $[\alpha]$ $= o'$	Concentration g./100 c.c.
0·4170 g.	718·9°	− 1·2°	Cd_{5086}	±720·1°	− 0·4°	719·7°	0·4290 g.
	648·3	+ 2·2	Cu_{5218}	646·2	+ 0·3	646·5	
	522·1	− 0·3	Hg_{5460}	522·4	+ 3·1	525·5	
	403·1	− 1·0	Hg_{5780}	404·1	+ 2·2	406·3	
	371·2	− 1·6	Na_{5812}	372·8	+ 1·7	374·5	
	333·7	+ 0·7	Li_{6103}	333·0	− 1·9	331·1	
	294·2	+ 1·1	Zn_{6362}	293·1	− 0·1	293·0	
	275·1	− 1·4	Cd_{6438}	276·5	+ 1·4	277·9	
	240·4	− 0·1	Li_{6707}	240·5	− 1·7	238·8	

TABLE III

5·nitro-o-toluidinomethylenecamphor in Benzene

$$[\alpha] = \pm \frac{66{\cdot}71}{\lambda^2 - 0{\cdot}16};\ \lambda_0 = 0{\cdot}4$$

Dextro			Line λ	Calc. [α] = *c*	*Lævo*		
Concentration g./100 c.c.	Obs. [α] = *o*	*o–c*			*o′–c*	Obs. [α] = *o′*	Concentration g./100 c.c.
0·4464 g.	675·5°	+ 1·0°	Cd_{5036}	±674·5	− 2·5°	672·0°	0·4224 g.
	595·4	+ 0·4	Cu_{5218}	595·0	− 2·7	592·3	
	479·4	− 0·6	Hg_{5460}	480	+ 1·7	481·7	
	380·8	− 0·2	Hg_{5780}	381	+ 0·7	381·7	
	357·2	+ 0·9	Na_{5812}	356·3	− 1·2	355·1	
	315·9	+ 1·7	Li_{6102}	314·2	+ 0·6	314·8	
	273·3	+ 2·0	Zn_{6362}	271·3	+ 0·2	271·5	
	254·2	+ 0·2	Cd_{6438}	254·0	+ 0·5	254·5	
	230·7	+ 0·7	Li_{6707}	230	− 2·8	227·2	

TABLE IV

5·nitro-o-toluidinomethylenecamphor in Ethyl Alcohol

$$[\alpha] = \pm \frac{67{\cdot}43}{\lambda^2 - 0{\cdot}163};\ \lambda_0 = 0{\cdot}4037$$

Dextro			Line λ	Calc. [α] = *c*	*Lævo*		
Concentration g./100 c.c.	Obs. [α] = *o*	*o–c*			*o′–c*	Obs. [α] = *o′*	Concentration g./100 c.c.
0·4204 g.	617·2°	− 0·1°	Cu_{5218}	±617·3	+ 1·7°	619°	0·4224 g.
	500·7	+ 0·7	Hg_{5460}	500	+ 0·6	500·6	
	396	+ 0·6	Hg_{5780}	395·4	− 2·4	393	
	366·3	+ 0·3	Na_{5812}	366	− 0·2	365·8	
	323	+ 1·2	Li_{6103}	321·8	+ 0·1	321·9	
	279·4	− 0·1	Zn_{6362}	279·5	− 2·5	277	
	264	− 0·2	Cd_{6438}	264·2	− 2·2	262	
	239	− 1·0	Li_{6707}	240	+ 0·2	240·2	

TABLE V

5·nitro-o-toluidinomethylenecamphor in Pyridine

$$[\alpha] = \pm \frac{70{\cdot}2}{\lambda^2 - 0{\cdot}173}\,;\ \lambda_0 = 0{\cdot}4159$$

Dextro			Line λ	Calc. [α] = *c*	*Lævo*		
Concentration g./100 c.c.	Obs. [α] = *o*	*o*–*c*			*o′*–*c*	Obs. [α] = *o′*	Concentration g./100 c.c.
0·4256 g.	701·3°	+ 1·1°	Cu_{5218}	±700·2	+ 0·4°	700·6°	0·4216 g.
	561·5	− 0·1	Hg_{5460}	561·6	− 1·6	560	
	436·1	+ 0·1	Hg_{5780}	436	+ 0·4	436·4	
	404·1	+ 1·1	Na_{5812}	403	+ 1·4	404·4	
	353·6	− 0·1	Li_{6103}	353·7	+ 2·0	355·7	
	301·9	− 0·9	Zn_{6362}	302·8	− 1·6	301·2	
	287·8	+ 1·2	Cd_{6438}	286·6	− 0·8	285·8	
	258·9	+ 2·5	Li_{6707}	256·4	− 0·3	256·1	

TABLE VI

5·nitro-o-toluidinomethylenecamphor in Chloroform

$$[\alpha] = \pm \frac{66{\cdot}63}{\lambda^2 - 0{\cdot}1707}\,;\ \lambda_0 = 0{\cdot}4131$$

Dextro			Line λ	Calc. [α] = *c*	*Lævo*		
Concentration g./100 c.c.	Obs. [α] = *o*	*o*–*c*			*o′*–*c*	Obs. [α] = *o′*	Concentration g./100 c.c.
0·4204 g.	753°	− 1·6°	Cd_{5086}	±754·6	+ 1·4°	756°	0·4556 g.
	646	− 0·8	Cu_{5218}	646·8	+ 0·7	647·5	
	523·3	− 0·2	Hg_{5460}	523·5	− 0·5	523	
	408	− 1·2	Hg_{5780}	409·2	+ 0·8	410	
	381·7	+ 1·2	Na_{5812}	380·5	− 1·8	378·7	
	331·8	+ 1·6	Li_{6103}	330·2	+ 0·1	330·3	
	291	− 1·2	Zn_{6362}	292·2	+ 1·9	294·1	
	281·9	+ 1·4	Cd_{6438}	280·5	+ 1·5	282	
	242·6	+ 2·8	Li_{6707}	239·8	+ 1·2	240	

TABLE VII

3·nitro-o-toluidinomethylenecamphor in Benzene

$$[\alpha] = \pm \frac{25 \cdot 33}{\lambda^2 - 0 \cdot 1648}; \lambda_0 = 0 \cdot 4060$$

Dextro			Line λ	Calc. $[\alpha] = c$	*Lævo*		
Concentration g./100 c.c.	Obs. $[\alpha] = o$	$o-c$			$o'-c$	Obs. $[\alpha] = o'$	Concentration g./100 c.c.
0·4012 g.	190·6°	+ 0·6°	Hg_{5460}	±190°	± 0 °	190°	0·4000 g.
	150·8	+ 0·8	Hg_{5780}	150	± 0	150	
	139·5	+ 0·8	Na_{5812}	138·7	± 0	138·7	
	122·1	+ 0·1	Li_{6103}	122	+ 0·5	122·5	
	108	+ 2·4	Zn_{6362}	105·6	+ 3·3	108·9	
	104	− 0·5	Cd_{6138}	104·5	+ 0·9	105·4	
	90·9	+ 1·4	Li_{6707}	89·5	+ 1·7	91·2	

TABLE VIII

3·nitro-o-toluidinomethylenecamphor in Acetone

$$[\alpha] = \pm \frac{29 \cdot 75}{\lambda^2 - 0 \cdot 1714}; \lambda_0 = 0 \cdot 4140$$

Dextro			Line λ	Calc. $[\alpha] = c$	*Lævo*		
Concentration g./100 c.c.	Obs. $[\alpha] = o$	$o-c$			$o'-c$	Obs. $[\alpha] = o'$	Concentration g./100 c.c.
0·4020 g.	184°	+ 1·0°	Hg_{5780}	±183°	+ 0·7°	183·7°	0·4028 g.
	167·6	− 1·6	Na_{5812}	169·2	− 0·4	168·8	
	148	+ 0·1	Li_{6103}	147·9	+ 1·0	148·9	
	136·8	− 0·7	Zn_{6362}	137·5	− 1·0	136·5	
	123·5	+ 1·2	Cd_{6438}	122·3	+ 1·9	124·2	
	109·4	+ 2·4	Li_{6707}	107	+ 2·2	109·2	

TABLE IX

3·*nitro*-o-*toluidinomethylenecamphor in Ethyl Alcohol*

$$[\alpha] = \pm \frac{27{\cdot}66}{\lambda^2 - 0{\cdot}1777}\,;\ \lambda_0 = 0{\cdot}4215$$

Dextro			Line λ	Calc. [α] = *c*	*Lævo*		
Concentration g./100 c.c.	Obs. [α] = *o*	*o*–*c*			*o′*–*c*	Obs. [α] = *o′*	Concentration g./100 c.c.
0·4032 g.	177·3°	+ 0·3°	Hg_{5780}	±177°	− 2·9°	175·9°	0·4036 g.
	162·4	− 0·7	Na_{5812}	163·1	− 2·1	161	
	142·6	+ 0·7	Li_{6103}	141·9	− 0·4	141·5	
	130·2	− 1·6	Zn_{6362}	131·8	− 0·5	131·3	
	119	+ 2·0	Cd_{6138}	117	+ 3·1	120·1	
	101·6	± 0	Li_{6707}	101·6	+ 1·2	102·8	

TABLE X

3·*nitro*-o-*toluidinomethylenecamphor in Methyl Alcohol*

$$[\alpha] = \pm \frac{28{\cdot}8}{\lambda^2 - 0{\cdot}1742}\,;\ \lambda_0 = 0{\cdot}4173$$

Dextro			Line λ	Calc. [α] = *c*	*Lævo*		
Concentration g./100 c.c.	Obs. [α] = *o*	*o*–*c*			*o′*–*c*	Obs. [α] = *o′*	Concentration g./100 c.c.
0·4060 g.	180°	± 0°	Hg_{5780}	±180°	− 1·6°	178·4°	0·4064 g.
	167·4	+ 1·0	Na_{5812}	166·4	+ 0·9	167·3	
	145·3	+ 0·3	Li_{6103}	145	+ 0·1	145·1	
	125·6	+ 0·6	Zn_{6362}	125	+ 1·7	126·7	
	120·6	+ 0·8	Cd_{6438}	119·8	+ 2·0	121·8	
	104·7	+ 0·3	Li_{6707}	104·4	+ 1·4	105·8	

TABLE XI

3·nitro-o-toluidinomethylenecamphor in Pyridine

$$[\alpha] = \pm \frac{29{\cdot}09}{\lambda^2 - 0{\cdot}1907}\ ;\ \lambda_0 = 0{\cdot}4367$$

Dextro			Line λ	Calc. $[\alpha] = c$	*Lævo*		
Concentration g./100 c.c.	Obs. $[\alpha] = o$	$o-c$			$o'-c$	Obs. $[\alpha] = o'$	Concentration g./100 c.c.
0·4026 g.	205°	+ 2·0°	Hg_{5790}	± 203°	+ 0·7°	203·7°	0·4024 g.
	188	+ 2·2	Na_{5812}	185·8	+ 1·8	187·6	
	160·5	+ 0·5	Li_{6103}	160	− 1·0	159	
	135	− 0·9	Zn_{6362}	135·9	− 0·5	135·4	
	128·5	− 1·5	Cd_{6438}	130	− 0·8	129·2	
	115	+ 2·8	Li_{6707}	112·2	+ 3·3	115·5	

TABLE XII

2: 5-toluylenebisaminomethylenecamphor in Benzene

$$[\alpha] = \pm \frac{90{\cdot}31}{\lambda^2 - 0{\cdot}1619}\ ;\ \lambda_0 = 0{\cdot}4023$$

Dextro			Line λ	Calc. $[\alpha] = c$	*Lævo*		
Concentration g./100 c.c.	Obs. $[\alpha] = o$	$o-c$			$o'-c$	Obs. $[\alpha] = o'$	Concentration g./100 c.c.
0·4092 g.	827·2°	+ 2·0°	Cu_{5218}	± 825·2°	+ 2·0°	827·2°	0·4092 g.
	661	− 2·1	Hg_{5460}	663·1	− 3·1	660	
	525·4	+ 0·6	Hg_{5780}	524·8	+ 3·0	527·8	
	488·8	+ 0·3	Na_{5812}	488·5	− 0·5	488	
	430·1	+ 1·3	Li_{6103}	428·8	+ 1·3	430·1	
	365·3	+ 0·8	Zn_{6362}	364·5	− 1·5	363	
	344·5	+ 0·4	Cd_{6438}	344·1	− 0·8	343·3	
	317·6	+ 2·0	Li_{6707}	315·6	− 0·4	315·2	

TABLE XIII

2 : 5-*toluylenebisaminomethylenecamphor in Acetone*

$$[\alpha] = \pm \frac{98 \cdot 36}{\lambda^2 - 0 \cdot 1624}\ ;\ \lambda_0 = 0 \cdot 4030$$

Dextro			Line λ	Calc. $[\alpha]$ $= c$	*Lævo*		
Concentration g./100 c.c.	Obs. $[\alpha]$ $= o$	$o-c$			$o'-c$	Obs. $[\alpha]$ $= o'$	Concentration g./100 c.c.
0·4012 g.	895·3°	+ 0·3°	Cu_{5218}	±895°	+ 1·3°	896·3°	0·4016 g.
	700	− 1·0	Hg_{5410}	701	− 1·0	700	
	550	− 1·2	Hg_{5780}	551·2	− 1·2	550	
	529·6	− 0·6	Na_{5812}	530·2	− 1·9	528·3	
	470·6	+ 2·5	Li_{6103}	468·1	+ 2·5	470·6	
	411·2	− 0·5	Zn_{6362}	411 7	+ 1·6	413·3	
	403·7	− 0·4	Cd_{6438}	404·1	+ 0·5	404·6	
	342·7	− 0·7	Li_{6707}	342	+ 1·6	343·6	

TABLE XIV

2 : 5-*toluylenebisaminomethylenecamphor in Chloroform*

$$[\alpha] = \pm \frac{97 \cdot 40}{\lambda^2 - 0 \cdot 1672}\ ;\ \lambda_0 = 0 \cdot 4089$$

Dextro			Line λ	Calc. $[\alpha]$ $= c$	*Lævo*		
Concentration g./100 c.c.	Obs. $[\alpha]$ $= o$	$o-c$			$o'-c$	Obs. $[\alpha]$ $= o'$	Concentration g./100 c.c.
0·4016 g.	936·2°	+ 0·2°	Cu_{5218}	±936°	+ 1·1°	937·1°	0·4008 g.
	739·5	− 1·5	Hg_{5460}	741	− 0·4	740·6	
	576·4	− 1·4	Hg_{5780}	577·8	− 0·3	577·5	
	540·3	− 0·8	Na_{5812}	541·1	+ 0·3	541·4	
	473·1	− 1·3	Li_{6103}	474·4	− 1·6	472·8	
	410·8	− 0·5	Zn_{6362}	411·3	+ 0·3	411·6	
	394·6	+ 0·9	Cd_{6438}	393·7	+ 0·5	394·2	
	348·6	+ 0·5	Li_{6707}	348·1	− 1·5	346·6	

TABLE XV

2: 5-toluylenebisaminomethylenecamphor in Ethyl Alcohol

$$[\alpha] = \pm \frac{89 \cdot 10}{\lambda^2 - 0 \cdot 1717} ; \lambda_0 = 0 \cdot 4143$$

Dextro			Line λ	Calc. $[\alpha] = c$	*Lævo*		
Concentration g./100 c.c.	Obs. $[\alpha] = o$	$o-c$			$o'-c$	Obs. $[\alpha] = o'$	Concentration g./100 c.c.
0·1964 g.	1025·9°	+ 0·6°	Cd_{5683}	± 1025·3°	+ 2·0°	1027·3°	0·1976 g.
	885·5	+ 0·5	Cu_{5218}	885	+ 0·6	885·6	
	725·5	+ 0·5	Hg_{5460}	725	− 1·3	723·7	
	567·7	− 0·2	Hg_{5780}	567·9	− 1·1	566·8	
	519·3	− 1·7	Na_{5812}	521	+ 0·2	521·2	
	455·7	− 0·4	Li_{6103}	456·1	+ 0·8	456·9	
	394·4	− 0·3	Zn_{6362}	394·7	− 1·2	393·5	
	368	+ 1·0	Cd_{6438}	367	+ 0·7	367·7	
	320·7	+ 0·7	Li_{6707}	320	+ 1·3	321·3	

TABLE XVI

2: 5-toluylenebisaminomethylenecamphor in Pyridine

$$[\alpha] = \pm \frac{98 \cdot 9}{\lambda^2 - 0 \cdot 1680} ; \lambda_0 = 0 \cdot 4099$$

Dextro			Line λ	Calc $[\alpha] = c$	*Lævo*		
Concentration g./100 c.c.	Obs. $[\alpha] = o$	$o-c$			$o'-c$	Obs. $[\alpha] = o'$	Concentration g./100 c.c.
0·2028 g.	948·2°	± 0°	Cu_{5218}	± 948·2°	+ 0·3°	948·5°	0·2040 g.
	761·8	+ 1·6	Hg_{5460}	760·2	+ 4·5	764·7	
	596·6	+ 0·8	Hg_{5780}	595·8	+ 2·2	598	
	552·2	+ 0·3	Na_{5812}	551·9	+ 3·1	554	
	478·3	− 3·3	Li_{6103}	481·6	− 3·6	478	
	426·5	− 1·5	Zn_{6362}	428	− 1·6	426·4	
	401·8	+ 0·6	Cd_{6438}	401·2	+ 0·8	402	
	345·1	− 3·6	Li_{6707}	348·7	− 3·1	345·6	

TABLE XVII

2 : 5-*toluylenebisaminomethylenecamphor in Methyl Alcohol*

$$[\alpha] = \pm \frac{101 \cdot 0}{\lambda^2 - 0 \cdot 1549}; \lambda_0 = 0 \cdot 3935$$

Dextro			Line λ	Calc. $[\alpha] = c$	*Lævo*		
Concentration g./100 c.c.	Obs. $[\alpha] = o$	$o-c$			$o'-c$	Obs. $[\alpha] = o'$	Concentration g. 100 c.c.
0·1216 g.	860°	− 0·9°	Cu_{5218}	±860·9°	+ 0·9°	861·8°	0·1224 g.
	694·9	− 0·4	Hg_{5460}	695·3	− 0·9	694·4	
	551	− 0·8	Hg_{5780}	551·8	− 1·2	550·6	
	522·2	− 3·0	Na_{5812}	525·2	− 3·2	522	
	460·5	− 0·3	Li_{6103}	460·8	+ 0·8	461·6	
	403·0	− 1·3	Zn_{6362}	404·3	+ 0·1	404·4	
	386·5	+ 1·4	Cd_{6438}	385·1	− 1·1	384	
	339·9	± 0	Li_{6707}	339·9	− 0·9	339	

TABLE XVIII

2 : 3-*toluylenebisaminomethylenecamphor in Acetone*

$$[\alpha] = \pm \frac{73 \cdot 73}{\lambda^2 - 0 \cdot 1259}; \lambda_0 = 0 \cdot 3549$$

Dextro			Line λ	Calc. $[\alpha] = c$	*Lævo*		
Concentration g./100 c.c.	Obs. $[\alpha] = o$	$o-c$			$o'-c$	Obs. $[\alpha] = o'$	Concentration g./100 c.c.
0·4060 g.	503·7°	+ 0·6°	Cu_{5218}	±503·1°	− 0·4°	502·7°	0·4048 g.
	420	+ 1·9	Hg_{5460}	418·1	+ 0·6	418·7	
	350·9	− 3·4	Hg_{780}	354·3	− 3·6	350·7	
	334·9	+ 1·9	Na_{5812}	333	+ 0·4	333·4	
	296·8	− 2·1	Li_{6103}	298·9	− 2·5	296·4	
	267·2	+ 2·8	Zn_{6362}	264·4	+ 2·4	266·8	
	258·6	+ 3·2	Cd_{6438}	255·4	+ 3·3	258·7	
	231	+ 3·5	Li_{6707}	227·5	+ 4·7	232·2	

TABLE XIX

2 : 3-*toluylenebisaminomethylenecamphor in Ethyl Alcohol*

$$[\alpha] = \pm \frac{62 \cdot 75}{\lambda^2 - 0 \cdot 1234}\ ;\ \lambda_0 = 0 \cdot 3513$$

Dextro			Line λ	Calc. $[\alpha] = c$	*Lævo*		
Concentration g./100 cc..	Obs. $[\alpha] = o$	$o-c$			$o'-c$	Obs. $[\alpha] = o'$	Concentration g./100 c.c.
0·4056 g.	421·6°	+ 0·6°	Cu_{5218}	±421°	− 0·3°	420·7°	0·4052 g.
	363·6	+ 2·9	Hg_{5460}	360·7	+ 3·3	364	
	303·2	+ 3·5	Hg_{5780}	299·7	+ 2·6	302·3	
	279·8	− 1·2	Na_{5812}	280	+ 0·1	280·1	
	249	− 2·7	Li_{6103}	251·7	− 3·7	248	
	225·2	+ 2·2	Zn_{6362}	223·0	+ 2·8	225·8	
	214·5	− 1·0	Cd_{6438}	215·5	− 0·8	214·7	
	181·2	− 1·5	Li_{6707}	182·7	− 0·1	182·6	

TABLE XX

2 : 3-*toluylenebisaminomethylenecamphor in Benzene*

$$[\alpha] = \pm \frac{52 \cdot 46}{\lambda^2 - 0 \cdot 1372}\ ;\ \lambda_0 = 0 \cdot 3704$$

Dextro			Line λ	Calc. $[\alpha] = c$	*Lævo*		
Concentration g./100 c.c.	Obs. $[\alpha] = o$	$o-c$			$o'-c$	Obs. $[\alpha] = o'$	Concentration g./100 c.c.
0·2360 g.	394·0°	− 1·2°	Cu_{5218}	±395·2°	− 0·4°	394·8°	0·2368 g.
	323·7	− 2·2	Hg_{5460}	325·9	− 2·9	323	
	271·2	+ 0·7	Hg_{5780}	270·5	+ 1·8	272·3	
	250	± 0	Na_{5812}	250	− 0·9	249·1	
	222·5	− 0·5	Li_{6103}	223	+ 0·7	223·7	
	197·0	+ 0·9	Zn_{6362}	196·1	+ 0·2	196·3	
	188·5	− 0·6	Cd_{6438}	189·1	− 1·1	188	
	167·3	− 0·4	Li_{6707}	167·7	− 0·9	166·8	

TABLE XXI

2: 3-*toluylenebisaminomethylenecamphor in Methyl Alcohol*

$$[\alpha] = \pm \frac{75{\cdot}93}{\lambda^2 - 0{\cdot}1144}; \quad \lambda_0 = 0{\cdot}3382$$

Dextro			Line λ	Calc. [α] = *c*	*Lævo*		
Concentration g./100 c.c.	Obs. [α] = *o*	*o*–*c*			*o′*–*c*	Obs. [α] = *o′*	Concentration g./100 c.c.
0·4032 g.	484·8°	+ 2·4°	Cu_{5218}	±482·4°	+ 0·9°	483·3°	0·4024 g.
	415·4	+ 2·1	Hg_{5460}	413·3	+ 1·7	415	
	344·7	− 1·0	Hg_{5780}	345·7	− 1·6	344·1	
	327·3	+ 1·2	Na_{5812}	326·1	+ 0·2	326·3	
	296·3	+ 1·8	Li_{6103}	294·5	+ 1·2	295·7	
	262·8	+ 1·3	Zn_{6362}	261·5	+ 1·9	263·4	
	252·9	− 0·1	Cd_{6438}	253	+ 0·4	253·4	
	220·7	− 1·6	Li_{6707}	222·3	− 1·2	221·1	

TABLE XXII

2: 3-*toluylenebisaminomethylenecamphor in Chloroform*

$$[\alpha] = \pm \frac{87{\cdot}28}{\lambda^2 - 0{\cdot}0937}; \quad \lambda_0 = 0{\cdot}3061$$

Dextro			Line λ	Calc. [α] = *c*	*Lævo*		
Concentration g./100 c.c.	Obs. [α] = *o*	*o*–*c*			*o′*–*c*	Obs. [α] = *o′*	Concentration g./100 c.c.
0·4032 g.	505·9°	+ 1·8°	Cu_{5218}	±504·1°	− 1·4°	503·7°	0·4020 g.
	427·8	+ 0·8	Hg_{5460}	427	− 1·6	426·6	
	359·6	− 0·6	Hg_{5780}	360·2	− 0·8	359·4	
	341	+ 1·0	Na_{5812}	340	− 0·5	339·5	
	313·7	+ 0·7	Li_{6103}	313	+ 0·4	313·4	
	280·7	+ 0·1	Zn_{6362}	280·6	− 1·0	279·6	
	267·4	− 0·8	Cd_{6438}	268·2	− 1·6	266·6	
	231·9	− 2·6	Li_{6707}	234·5	− 2·0	232·5	

TABLE XXIII

2 : 3 *-toluylenebisaminomethylenecamphor in Pyridine*

$$[\alpha] = \pm \frac{96 \cdot 2}{\lambda^2 - 0 \cdot 0912}; \lambda_0 = 0 \cdot 3020$$

Dextro			Line λ	Calc. $[\alpha] = c$	*Lævo*		
Concentration g./100 c.c.	Obs. $[\alpha] = o$	$o-c$			$o'-c$	Obs. $[\alpha] = o'$	Concentration g./100 c.c.
0·4048 g.	543°	+ 1·8°	Cu_{5218}	±541·2°	+ 3·1°	544·3°	0·4060 g.
	466·9	+ 1·9	Hg_{5460}	465	+ 0·9	465·9	
	395·2	− 1·0	Hg_{5780}	396·2	+ 0·3	396·5	
	376	+ 1·2	Na_{5812}	375·2	+ 1·6	376·8	
	340·9	− 1·0	Li_{6103}	341·9	+ 0·4	342·3	
	305	+ 1·4	Zn_{6362}	303·6	+ 1·8	305·4	
	295·2	− 2·3	Cd_{6138}	297·5	− 2·0	295·5	
	258·1	− 0·3	Li_{6707}	258·4	+ 0·2	258·6	

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ON NORMAL NUMBERS

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§1. *Introduction*

Let $F(m, R, b, x)$ denote the number of times that the digit b occurs in the first m places when the fractional part of x is expressed in the scale of R. If $F(m, R, b, x)/m \to 1/R$ for every $b < R$, then x is said to be *simply normal* in the scale of R.

Definition A: If x is simply normal in all the scales, $r, r^2, r^3, \ldots$, then x is *normal* in the scale of r.

Definition B: If all the numbers $x, rx, r^2x, \ldots$ are simply normal in all the scales $r, r^2, r^3, \ldots$, then x is *normal* in the scale of r.

In a sample page of the '*Mathematics Review*' it was pointed out that my proof[1] of a theorem of Champernowne's was inadequate. Further, Dr. Vijayaraghavan, by giving an example[2], suggested that my remark, about definition B, that it seemed to contain superfluous conditions,[2] might not be correct.

This paper owes its origin to the above remarks. In this paper, I make the proof adequate and prove that the two definitions are equivalent. So we may take the simpler definition A.

Further Notations and Symbols

Unless otherwise mentioned, the scale of notation is 10.

Let $x+1, x+2, \ldots, x+q$ be q consecutive integers of l digits, and X stand for any of these numbers. $K = a_1 a_2 \ldots a_{ql}$ is the number that we get when we write down $x+1, \ldots, x+q$ one after another in the same

[1] *Proc. Ind. Acad. Sci.*, 1939, **10**, No. 1.

[2] If $a_1 = 22$, $a_2 = 12$, $a_3 = 13$, and $a_4, a_5, \ldots, a_{100}$ are other 97 numbers less than 100, and $x = \cdot \overset{*}{a}_1 a_2 \ldots \overset{*}{a}_{100}$, then $10x = 2 \cdot \overset{*}{b}_1 b_2 \ldots \overset{*}{b}_{100}$, where $b_1 = 21$, $b_2 = 21, \ldots$ Since 21 occurs twice, $10x$ is not simply normal, but x is simply normal in the scale of 100. It is understood that if $a_r = 0, 1, \cdot\cdot$, or 9, then it should be written as 00, 01, $\cdot\cdot\cdot$, or 09.

order. $b = a_1\ a_2 \ldots a_k$ is a fixed number of k digits, where even a_1 may be equal to zero.

Arrange $x+1, \ldots, x+q$ one below the other as

$$\begin{array}{l} x+1 \\ x+2 \\ \cdots\cdots \\ \cdots\cdots \\ x+q. \end{array}$$

There are q rows and l digits in each row. $b_{t,s}$ stands for the b (if any) which begins at the tth column and the sth row, where $t \leqslant l-k+1$. This $b_{t,s}$ will occur as a group of k digits in K. $\mathrm{P}(b_{t,s})$ denotes the number of digits in K to the left of $b_{t,s}$.

$$d = (l, k);\ \mathrm{D} = k/d;\ l = de; \tag{1}$$

$\mathrm{G}_h(x+q+1, x+1)$ = the total number of $b_{t,s}$ which occur in K and for which $\mathrm{P}(b_{t,s}) \equiv h \pmod{k}$. $\mathrm{M} = \cdot 123 \ldots \mathrm{N}$, where 1, 2, . . ., N are the positive integers in order.

$\mathrm{Q}(\mathrm{M})$ = the number of digits in M when M is expressed in the scale of 10^k.

$\mathrm{R}(\mathrm{M}) = \mathrm{R}(b, \mathrm{M}) = \mathrm{R}(b, \mathrm{M}, 10^k)$ denotes the number of times that the digit b occurs when M is expressed in the scale of 10^k.

$$n = [\log \mathrm{N}/\log 10] \tag{2}$$

$\mathrm{E}(\mathrm{N})$ = the total number of digits in all the numbers $\leqslant \mathrm{N}$, in the scale of 10^k.

$\theta = \cdot 1234567891011 \ldots$, where 1, 2, 3, . . . are the positive integers in order.

Proof of Champernowne's Theorem

Lemma 1: $\mathrm{P}(b_{t,u}) \equiv \mathrm{P}(b_{t,v}) \pmod{k}$ if and only if $u \equiv v \pmod{\mathrm{D}}$. $\mathrm{P}(b_{t,u}) - \mathrm{P}(b_{t,v}) = (u-v)\,l = (u-v)\,de$, where $(e, k) = 1$.

Lemma 2: $\mathrm{P}(b_{t+1,u}) \equiv \mathrm{P}(b_{t,v}) + 1 \pmod{d}$

$\mathrm{P}(b_{t+1,u}) - \mathrm{P}(b_{t,v}) = 1 + (u-v)\,l$.

Lemma 3: $\mathrm{P}(b_{t,u}) \equiv \mathrm{P}(b_{s,v}) \pmod{d}$ if and only if $t \equiv s \pmod{d}$. This follows from lemma 2.

Lemma 4: $\mathrm{G}_h(x+q+1, x+1) = ql/(k \cdot 10^k) + \mathrm{O}(10^l)$.

X will have b as $b_{t,s}$ if and only if $\mathrm{X} = x+s$

and $m \cdot 10^{l-t+1} + b \cdot 10^{l-t-k+1} \leqslant \mathrm{X} < m \cdot 10^{l-t+1} + (b+1)\,10^{l-t-k+1}$.

So there will be $q/10^{l-t+1}+\mathrm{O}(1)$ groups of $10^{l-t-k+1}$ consecutive integers containing b as $b_{t,s}$. (3)

From lemma 1, if $10^{l-t-k+1}$ consecutive integers X contain b as $b_{t,s}$, then the number of numbers in the above for which $\mathrm{P}(b_{t,s}) \equiv h \pmod{k}$ is $10^{l-t-k+1}/\mathrm{D}+\mathrm{O}(1)$. (4)

From (3), (4), when t is fixed, the number of X for which $\mathrm{P}(b_{t,s}) \equiv h \pmod{k}$ is

$$\{10^{l-t-k+1}/\mathrm{D}+\mathrm{O}(1)\}\ \{q/10^{l-t+1}+\mathrm{O}(1)\}$$

$$= q/(\mathrm{D}\cdot 10^k)+\mathrm{O}\{10^{l-t-k}+q/10^{l-t}\}. \tag{5}$$

From lemma 3, $\mathrm{P}(b_{t,s}) \equiv h \pmod{k}$ only for $l/d+\mathrm{O}(1)$ values of t. (6)

From (5), (6),

$$\mathrm{G}_h(x+q+1,\ x+1) \geqslant \sum_t \{q/(\mathrm{D}\cdot 10^k)+\mathrm{O}(10^{l-t-k}+q/10^{l-t}\}$$

$$= \{q/(\mathrm{D}\cdot 10^k)\ \{l/d+\mathrm{O}(1)\}+\mathrm{O}(10^l)+\mathrm{O}(q)$$

$$= ql/(k\cdot 10^k)+\mathrm{O}(10^l);$$

for $q=\mathrm{O}(10^l)$. (7)

If $a_1, \ldots, a_u$ and $a_{u+1}, \ldots, a_k$ occur at the end of X and the beginning of X + 1 respectively, then this will give rise to one b in K. But a particular X and X + 1 cannot give rise to such a broken b more than k times as $(a_1, a_2 \ldots a_k)$, $(a_1\ a_2,\ a_3 \ldots a_k)$, $\ldots$, $(a_1 \ldots a_{k-1},\ a_k)$. Hence the number of b's (in K) which occur broken in A cannot exceed $k\,q$.

But (7) contains all the b's (in K) for which $\mathrm{P}(b_{t,s}) \equiv h \pmod{k}$, and which occur unbroken in A.

Hence $$\mathrm{G}(x+q+1,\ x+1) \leqslant q\,l/(k\cdot 10^k)+\mathrm{O}(10^l)+kq$$

$$= q\,l/(k\cdot 10^k)+\mathrm{O}(10^l) \tag{8}$$

From (7) and (8), the lemma follows:

Lemma 5: $\mathrm{R}(\mathrm{M}) = \mathrm{N}\,n/(k\cdot 10^k)+\mathrm{O}(\mathrm{N})$.

If $\mathrm{M} = \cdot d_1\,d_2\,d_3 \ldots\ldots$, in the scale of 10,

then $\mathrm{M} = \cdot c_1\,c_2\,c_3 \ldots\ldots$, in the scale of 10^k,

where $c_s = d_{(s-1)\,k+1} \ldots d_{sk}$.

Hence, $\mathrm{R}(\mathrm{M}) = \mathrm{G}_{h_1}(\mathrm{N}, 10^n)+\mathrm{G}_{h_2}(10^n, 10^{n-1})+\mathrm{G}_{h_3}(10^{n-1}, 10^{n-2})+\ \ldots$;
where $h_1, h_2, \ldots$ are suitable residue classes (mod. k).

Therefore, from lemma 4,

$$R(M) = (N - 10^n)(n+1)/(k \cdot 10^k) + O(10^n) + (10^n - 10^{n-1})\, n/(k \cdot 10^k) + O(10^{n-1}) + \ldots .$$

$$= \frac{1}{k \cdot 10^k}\{(N - 10^n)(n+1) + (10^n - 10^{n-1})\, n + \ldots\} + O\{10^n + 10^{n-1} + \ldots\}$$

$$= k^{-1} \cdot 10^{-k}\{n \cdot N + N - 10^n - 10^{n-1} + \ldots .\} + O(10^n) = n\, N/(k \cdot 10^n) + O(N).$$

Lemma 6: $Q(M) = N\, n/k + O(N)$.

If $r^{t-1} \leqslant x < r^t$, x contains t digits when it is expressed in the scale of r. So if $p = [n/k]$,

$$Q(M) = E(N) = E(N) - E(10^{pk}) + E(10^{pk}) - E(10^{pk-k}) + \ldots .$$
$$= (N - 10^{pk})(p+1) + (10^{pk} - 10^{pk-k}) \cdot p + \ldots .$$
$$= p\, N + O(N) = N\, n/k + O(N).$$

Lemma 7: $F(m, 10^k, b, \theta)/m \to 1/10^k$ when $m \to \infty$.

Given m, we can choose N so that

$$E(N) \leqslant m < E(N+1).$$

Since the number of digits in $N = O(\log N) = O(n)$,

$$m = E(N) + O(n),$$

and
$$F(m, 10^k, b, \theta) = R(M) + O(n).$$

Hence, from lemmas 5, 6,

$$\frac{F(m, 10^k, b, \theta)}{m} = \frac{N\, n/(k \cdot 10^k) + O(N) + O(n)}{N\, n/k + O(N) + O(n)}$$

$$= \frac{1/10^k + O(1/n)}{1 + O(1/n)} \to 1/10^k \text{ when } n \to \infty.$$

So the lemma is proved.

Lemma 7 means that θ is simply normal in the scale of 10^k for every k. So we get Champernowne's

THEOREM: θ is normal in the scale of 10.*

Equivalence of the Two Definitions

Lemma 8: If x is simply normal in the scale of r^{kt}, then

$$\frac{1}{t} + \frac{1}{r^k} \geqslant \overline{\lim}\, \frac{F(M, r^k, b, r^c x)}{M} \geqslant \underline{\lim}\, \frac{F(M, r^k, b, r^c x)}{M} \geqslant (1 - 1/t)/r^k,$$

where k, t, c, r and b are fixed and $b < r^k$.

*We have proved the result according to definition A. If we want to prove it according to definition B, the only alteration required is that instead of M we should take 10^c M, where c is any positive integer.

Let $b = a_1 a_2 \ldots a_k$ in the scale of r;

$g_l = d_1 \ldots d_{kl+c}\, a_1 \ldots a_k\, d_{(l+1)\,k+c+1} \ldots d_{kt}$ „ „ r;

$\{x\} = \cdot a_1 a_2 a_3 \ldots\ldots$ „ „ r,

$= \cdot A_1 A_2 A_3 \ldots\ldots$ „ „ r^{kt};

$\{r^c x\} = \cdot a_{c+1} a_{c+2} \ldots\ldots$ „ „ r,

$= \cdot B_1 B_2 B_3 \ldots\ldots$ „ „ r^k,

and $$T = \frac{1}{m} \sum_{l=0}^{t-2} \sum_{g_l} F(m, r^{kt}, g_l, x).$$

When l is fixed and $0 \leqslant l \leqslant t-2$, the number of different values for g_l is equal to $r^{k(t-1)}$.

Therefore, since x is simply normal in the scale of r^{kt} and $g_l < r^{kt}$,

$$T \sim \sum_{l=0}^{t-2} \sum_{g_l} \frac{1}{r^{kt}} = \frac{(t-1)\, r^{k(t-1)}}{r^{kt}} = \frac{t-1}{r^k}. \tag{9}$$

If $0 \leqslant l \leqslant t-2$ and $A_p = g_l$, then $B_{pt+l} = b$ and *vice versa*.

Hence $$\frac{F(m\,t, r^k, b, r^c x)}{m\,t} \geqslant \frac{1}{m\,t} \sum_{l=0}^{t-2} \sum_{g_l} F(m, r^{kt}, g_l, x)$$

$$= \frac{T}{t} \sim \left(1 - \frac{1}{t}\right) / r^k. \tag{10}$$

$B_{pt+t-1} = b$ if and only if the last $k-c$ digits in A_p are $a_1, a_2, \ldots, a_c$ and the first c digits in A_{p+1} are $a_{c+1}, \ldots, a_k$.

So $$\frac{F(m\,t, r^k, b, r^c x)}{m\,t} \leqslant \frac{T}{t} + \frac{1}{m\,t} \sum_{g_t - 1} F(m, r^{kt}, g_{t-1}, x). \tag{11}$$

When $l = t-1$, the number of different values for $g_{t-1} = r^{kt-c} \leqslant r^{kt}$.

Therefore, from (11),

$$\frac{F(m\,t, r^k, b, r^c x)}{m\,t} \leqslant \frac{T}{t} + \frac{r^{kt}}{m\,t} \times F(m, r^{kt}, g_{t-1}, x)$$

$$\sim \left(1 - \frac{1}{t}\right) / r^k + \frac{1}{t}. \tag{12}$$

From (10), (12), the lemma follows:

Lemma 9: Definition A implies definition B.

From definition A, if k and t are any two positive integers, x is simply normal in the scale of r^{kt}. Hence, from lemma 8, if c is any positive integer,

$$\frac{1}{t} + \frac{1}{r^k} \geqslant \overline{\lim} \frac{F(M, r^k, b, r^c x)}{M} \geqslant \underline{\lim} \frac{F(M, r^k, b, r^c x)}{M} \geqslant \left(1 - \frac{1}{t}\right) / r^k,$$

where $b < r^k$.

Since the above inequalities are true for every positive integer t, it follows that

$$\lim_{M \to \infty} \frac{F(M, r^k, b, r^c x)}{M} = 1/r^k.$$

This means that $r^c x$ is simply normal in the scale of r^k.

From this, the lemma follows:

Definition B obviously implies definition A. From this and lemma 9, we get

THEOREM II: The two definitions are equivalent.

Conclusion

By elaborating the argument for Theorem I, we can prove Theorems II, III, IV, V in my paper referred to. Theorem VI is also true. I do not find any necessity to modify the conjectures given there.

MOLECULAR STRUCTURE OF SOME SELENIUM COMPOUNDS DETERMINED BY MAGNETIC METHOD

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The use of the magnetic method for determining the molecular structure is based on Pascal's investigations who showed that the susceptibility of a molecule (χ_m) can be calculated from the atomic susceptibilities of the constituent atoms (χ_A) and the constitutive constant (λ) for different bindings. Also Bhatnagar and co-workers[1] have shown that in electrovalent salts, in which the ions have complete inert gas configuration the molecular susceptibility can be considered to be the sum of the susceptibilities of ions which constitute the molecule.

Pascal and Kido's experimental data provide the values of susceptibilities for a number of ions and atoms and for various types of bindings. In cases wherein they are not known they can be worked out, for diamagnetic atoms or ions, from Langevin equation

$$\chi_A = -a \Sigma_n \bar{r^2}$$

where $\Sigma_n \bar{r^2}$ is a function of the valency state of the ion and 'a' is a constant, equal to $\frac{e^2 z}{6mc^2}$. The mode of calculation of the value of $\Sigma \bar{r^2}$ is shown in the discussion of this paper.

The magnetic method has been employed by Farquharson[2] to determine the change in polarity of some of the linkages. Gray and Cruickshank[3] determined from the additivity law the depression in susceptibility due to various chemical bonds and used the data thus obtained to calculate the susceptibilities of several organic compounds. From the close agreement between the theoretical and experimental values they showed that the magnetic method can be employed not only to determine the structure of compounds but also to differentiate between isomeric structures and those which involve resonance. The same plan was employed by Clow[4] to elucidate the structure or urea and its several derivatives. He showed that a change in the parent molecule from a resonating zwitterion in urea itself through an amino-imino structure in N-monosubstituted urea to carbamide

in tetra-substituted molecules takes place, and that when there is a C: :N group in the molecule, it resonates between the structure C: :N̈ : and C⁺: N̈⁻: ·

Bhatnagar and Bahl[5] measured the magnetic susceptibilities of a large number of trivalent bismuth salts and on applying Pascal's law calculated the ionic susceptibility of Bi^{+3} which is in agreement with that calculated from Pauling's theoretical consideration. In the same manner Bhatnagar and Khanna[6] determined from its several salts the ionic susceptibility of rubidium which agrees with the theoretically calculated value. Bhatnagar, Nevgi and Sharma[7] determined the ionic susceptibilities of tin in di- and tetra-valent states and Bhatnagar, Prakash and Hamid[8] and Bhatnagar, Prakash and Maheswari[9] fixed up the valency states of chromium and manganese in their several compounds.

Varadachari and Subramaniam[10] have determined the susceptibilities of a number of sulphur compounds and by comparing their experimental values with those obtained on theoretical considerations have assigned proper valencies to sulphur in these compounds. Selenium belongs to the same group as sulphur and, like sulphur, though normally bivalent, can acquire more than one valency state.

An attempt has been made in this investigation to employ the magnetic method for the elucidation of the much debated molecular constitution of some of the selenium compounds in which Se may exist in several valency states. The molecular constitutions found by this method have been discussed along with the already known constitutions for these substances.

Experimental

The measurements of the magnetic susceptibilities were made by the modified form of Gouy's balance[11] and calculated by the usual formula,

$$\chi_{d_2} = \frac{1}{m d_2}\left[(\chi_{d_1} m_{d_1} - \chi_a m_{ad_1})\frac{pd_2}{pd_1} + \chi_a m_{ad_2}\right]$$

where

χ_{d_2} = magnetic susceptibility of the specimen being investigated,
m_{d_2} = mass of the substance under investigation,
χ_{d_1} = magnetic susceptibility of the standard substance,
m_{d_1} = mass of the standard substance,
χ_a = magnetic susceptibility of the medium which is air,
m_{ad_1} = mass of air displaced by the standard substance,
p_{d_1} = decrease in weight due to the standard substance,
and p_{d_2} = decrease in weight due to the specimen under investigation.

Kahlbaum's extra pure potassium chloride (magnetic susceptibility = $-0{\cdot}516 \times 10^{-6}$) was used as the standard substance. All the necessary precautions for the use of the apparatus were taken. To test the working of the apparatus the susceptibilities of pure substances from Kahlbaum were measured. The results obtained are given in Table I.

TABLE I

Substance	$-\chi_a \times 10^6$ observed	$-\chi_a \times 10^6$ from other authors
Potassium persulphate	0·371	0·3748 *Int. Crit. Tab.*
Selenium	0·322	0·320 ,,
Tellurium	0·323	0·320 ,,
Barium sulphate	0·306	0·306 ,,
Glycerine	0·538	0·538 ,,

Results

The magnetic susceptibilities obtained for the selenium compounds are given in Table II. These values are the mean of three independent observations.

TABLE II

Substance	Molecular formula	$\chi_a \times 10^6$	$\chi_m \times 10^6$
Selenium monobromide	Se_2Br_2	−0·3544	−112·8
Selenium monochloride	Se_2Cl_2	−0·4134	− 94·79
Selenious acid	H_2SeO_3	−0·3515	− 45·41
Silver selenite	Ag_2SeO_3	−0·293	−102·2
Selenosyl chloride	$SeOCl_2$	−0·2929	− 48·65

All the Selenium compounds except silver selenite were obtained either from Kahlbaum or from Theoder Schuchardt and were of extra pure quality. Silver selenite was prepared in the laboratory by adding selenious acid to an aqueous solution of silver nitrate. The Selenite, precipitated out as a white powder, was crystallised from a dilute solution of nitric acid and the crystals obtained in the form of long needles were analysed (Ag found = 62·77%; theory requires 62·90%).

Discussion of Results

Langevin Equation assumes the form $\chi_a = -2{\cdot}832 \times 10^{10} \Sigma_n \bar{r}^2$, when the values of the known constants are substituted. Van Vleck[12] and Pauling[13] have independently derived a quantum mechanical expression whereby χ for a single electron is given by

$$\chi = -0{\cdot}79 \times 10^{-6} \left\{ \tfrac{5}{2} n^2 - \frac{3l(l+1)-1}{2} \right\}.$$

The application of this expression has been extended by Pauling who by introducing appropriate screening constants for each (n, l) group of electrons, finds that

$$\chi_{nl} = -0{\cdot}79 \times 10^{-6} \frac{2l(l+1)n^2}{(z-\sigma_{nl})} \left\{ \tfrac{5}{2} n^2 - \frac{3l(l+1)-1}{2} \right\}.$$

The susceptibility of an atom or of an ion can be obtained by summing over all the sub-groups present in the atom or the ion.

An approximate method for the calculation of the value of $\Sigma \bar{r}^2$ has been more recently attempted by Slater[14] for a limited number of atoms. He takes the radial part of the curve function due to a single electron and finds that

$$\bar{r}^2 = \frac{(n')^2 (n' + \frac{1}{2})(n'+1)}{(z-s)^2}$$

where n' and $(z-s)$ are, respectively, the effective quantum number and the effective nuclear charge. The susceptibility obtained by summing over all the electrons, is given by

$$\chi_A \times 10^6 = -0{\cdot}79 \Sigma \frac{(n')^2 (n' + \frac{1}{2})(n'+1)}{(z-s)^2}.$$

Similar rules have been given by Slater for calculating the values of $(z-s)$ and (n') for any electronic group.

Values for $\Sigma \bar{r}^2$ and ionic susceptibilities for Se in various valency states have been calculated as described above and the results obtained are given in Table III. Angus[15] has introduced a slight modification in Slater's method for calculating the screening constant. Slater takes the s and p electrons together while Angus takes them separately. Results obtained according to Angus give lower values, as in this case, the effective charge for s electrons is increased. Consequently better agreement is obtained for heavier atoms, in which case Slater's method yields values which are a bit too high, while it is impaired in the case of lighter atoms. Values of $\Sigma \bar{r}^2$ and ionic susceptibilities calculated according to Angus are also given in Table III.

TABLE III

Diamagnetic Susceptibilities of Se *in Various Valency States Calculated from Various Methods*

Valency states	$\Sigma \bar{r^2}$ calculated by Slater's method	$-\chi \times 10^6$ calculated by Slater's method	$\Sigma \bar{r^2}$ calculated by modification in Slater's method	$-\chi \times 10^6$ calculated by modification in Slater's method, using constant 0·790 instead of 0·807	$\Sigma \bar{r^2}$ calculated by Angus's method	$-\chi \times 10^6$ calculated by Angus's method	$\Sigma \bar{r^2}$ calculated by modification in Angus's method	$-\chi \times 10^6$ calculated by modification in Angus's method using constant 0·790 instead of 0·807
Se divalent ..	28·32	22·86	34·59	27·32	26·75	21·59	32·09	25·34
Se tetravalent	17·60	14·20	19·18	15·15	17·52	14·14	16·10	15·09
Se hexavalent	9·85	7·95	8·61	6·800	9·77	7·881	8·52	6·732

The values of $\Sigma \bar{r^2}$ and ionic susceptibilities have also been calculated after introducing slight empirical changes, as given below, in Slater's and Angus's formulæ;

(A) giving the value 0·85 to the lower groups and not to the shells while calculating the screening constants,

(B) making no distinction between the *d* and *f* groups as compared with the ones containing *s* and *p*,

(C) taking 0·790 (given by Slater) instead of 0·807 (given by Angus).

These values have been employed in the discussion of the molecular constitution of different compounds and have been represented as follows:

$(\chi_a)_1$ and $(\chi_m)_1$ .. Specific and molecular susceptibilities in different states calculated according to Slater's method.

$(\chi_a)_2$ and $(\chi_m)_2$ .. Specific and molecular susceptibilities in different states calculated according to the modifications in Slater's method.

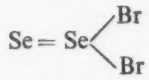
$(\chi_a)_3$ and $(\chi_m)_3$ .. Specific and molecular susceptibilities in different states calculated according to Angus's method.

$(\chi_a)_4$ and $(\chi_m)_4$ .. Specific and molecular susceptibilities in different states calculated according to the modifications of Angus's method.

$(\chi_a)_E$ and $(\chi_m)_E$ .. Experimental values of the author.

$(\chi_a)_0$ and $(\chi_m)_0$ .. Values observed by others.

1. *Selenium monobromide* (Se_2Br_2).—The constitution of this compound may be formulated as



(I)

or Br–Se–Se–Br (II)

Reactions of this substance with organic compounds, notably Grignard reagent, indicate that these two forms are likely to co-exist, thus representing an example of inorganic tautomerism (Morgan and Burstall, *Inorganic Chemistry*, p. 170). The calculated and the experimental magnetic values for the two constitutions are given in the following Table. In these calculations the value for Br^- ion is taken as $-32{\cdot}5 \times 10^{-6}$ (Stoner, *Magnetism and Matter*, p. 468).

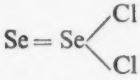
TABLE IV

Constitutional formula	(I)	(II) Br–Se–Se–Br
$(\chi_a)_1$	$-0{\cdot}3208 \times 10^{-6}$	$-0{\cdot}3479 \times 10^{-6}$
$(\chi_m)_1$	$-102{\cdot}06 \times 10^{-6}$	$-110{\cdot}72 \times 10^{-6}$
$(\chi_a)_2$	$-0{\cdot}3379 \times 10^{-6}$	$-0{\cdot}3574 \times 10^{-6}$
$(\chi_m)_2$	$-107{\cdot}47 \times 10^{-6}$	$-119{\cdot}64 \times 10^{-6}$
$(\chi_a)_3$	$-0{\cdot}3163 \times 10^{-6}$	$-0{\cdot}3400 \times 10^{-6}$
$(\chi_m)_3$	$-100{\cdot}73 \times 10^{-6}$	$-108{\cdot}18 \times 10^{-6}$
$(\chi_a)_4$	$-0{\cdot}3313 \times 10^{-6}$	$-0{\cdot}3636 \times 10^{-6}$
$(\chi_m)_4$	$-105{\cdot}43 \times 10^{-6}$	$-115{\cdot}68 \times 10^{-6}$
$(\chi_a)_5$		$-0{\cdot}3544 \times 10^{-6}$
$(\chi_m)_5$		$-112{\cdot}6 \times 10^{-6}$

It is clear from the above that all the calculated values of χ_a and χ_m for the constitution II agree fairly well with the experimental values. Hence the constitution of Se_2Br_2 is Br–Se–Se–Br.

This constitution is in agreement with the fact that organo-selenium compounds obtained as a result of the reaction between selenium monobromide and organo-magnesium compounds have a chain structure, –Se–Se–, (*cf.* Pieroni and Coli, *Gazzetta*, 1914, **44**, 349; Pieroni and Balduzzi, *ibid.*, 1915, **45**, 106).

2. *Selenium monochloride* (Se_2Cl_2).—It has been definitely shown by cryoscopic measurements of solutions of selenium monochloride in ethylene di-bromide that its molecular weight is in accordance with the molecular formula Se_2Cl_2 (Beckmann, *Zeit. anorg. chem.*, 1908, **63,** 63). However, its constitution is still uncertain. Its constitution may be represented either as

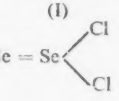


(I)

or Cl–Se–Se–Cl (II)

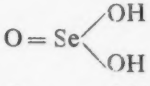
The calculated and experimental values for the two constitutions are given in the following Table. The value for Cl^- ion used in these calculations is taken as $-22{\cdot}2 \times 10^{-6}$ (Leiterer, *Z. physical chem.*, (B), 1937, **36,** 332; Bhatnagar, Prakash and Hamid, *Jour. Chem. Soc.*, 1938, 1433).

TABLE V

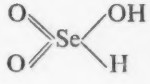
Constitutional formula	(I) 	(II) Cl–Se–Se–Cl
$(\chi a)_1$	$0{\cdot}3552 \times 10^{-6}$	$-0{\cdot}3930 \times 10^{-6}$
$(\chi m)_1$	$-81{\cdot}46 \times 10^{-6}$	$-90{\cdot}12 \times 10^{-6}$
$(\chi a)_2$	$-0{\cdot}3788 \times 10^{-6}$	$-0{\cdot}4319 \times 10^{-6}$
$(\chi m)_2$	$-86{\cdot}87 \times 10^{-6}$	$-99{\cdot}04 \times 10^{-6}$
$(\chi a)_3$	$-0{\cdot}3494 \times 10^{-6}$	$-0{\cdot}3819 \times 10^{-6}$
$(\chi m)_3$	$-80{\cdot}13 \times 10^{-6}$	$-87{\cdot}58 \times 10^{-6}$
$(\chi a)_4$	$-0{\cdot}3700 \times 10^{-6}$	$-0{\cdot}4145 \times 10^{-6}$
$(\chi m)_4$	$-84{\cdot}83 \times 10^{-6}$	$-95{\cdot}04 \times 10^{-6}$
$(\chi a)_E$		$-0{\cdot}4134 \times 10^{-6}$
$(\chi m)_E$		$-94{\cdot}79 \times 10^{-6}$

The above results show a good agreement for the constitution Cl–Se–Se–Cl and thus establish a similarity in the constitution of Se_2Cl_2 and Se_2Br_2.

3. *Selenious acid* (H_2SeO_3).—Nothing is definitely known regarding the constitution of selenious acid. Two possible structures are given below:



(I)



(II)

In (I) selenium is quadrivalent and both Hydrogen atoms belong to hydroxyl groups while in (II) selenium is hexavalent. The acid is classed amongst the pseudo acids in which changes can take place in their constitution. Karve[16] has studied the absorption spectra and the catalytic activity of this acid and has concluded that it is an associated pseudo acid in the pure condition. The aqueous solution of the acid contains large proportion of the pseudo acid and only a small percentage of the hydrate of the true acid.

One may take the nonformation of a selenium analogue of thiosulphuric acid on heating selenium with a selenite solution as an evidence in favour of the formula I. This view is also supported by the formation of ethyl selenite $O=Se\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix}$ by the action of (*i*) sodium ethoxide on selenosyl chloride and (*ii*) ethyl iodide on silver selenite (Michaelis and Landmann, *Ber.*, 1880, **13**, 656; 1887, **20**, 625).

Recently the constitution of this compound has been investigated by Venkateswaran[17] who studied Raman spectra of the solid crystalline acid and of its aqueous and alcoholic solutions of varying concentrations. He also studied the Raman spectra of sodium biselenite and sodium selenite. His results point to the existence of both types of molecules, namely, the forms (I) and (II), in dynamical equilibrium with each other. In the solid state and in solution in methyl alcohol the form (II) is predominant while in aqueous solution almost the whole of the acid exists in the form (I). This shows that in the solid state selenium is hexavalent and in aqueous solutions it is tetravalent.

The results given in the Table below refer to solid selenious acid. In order to calculate the magnetic susceptibility of this acid the following values for the groups present are used.

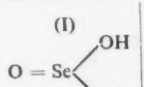
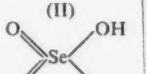
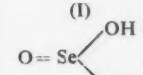
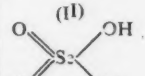
$$OH = -7{\cdot}54 \times 10^{-6} \text{ (Pascal)}.$$

$$H = -3{\cdot}05 \times 10^{-6} \text{ (}\textit{Int. Crit. Tab.}\text{)}$$

and the results obtained are given under A of Table VI.

Although there is a very good agreement between the author's experimental value and that given in the *International Critical Tables* it will be seen that it does not agree with any of the calculated values. This discrepancy may be due to oxygen atoms whose atomic susceptibility varies with the mode of combination. If binding between oxygen and other atoms is strong, it produces ionic deformation and consequently introduces a high paramagnetic term in the total molecular susceptibility. The ionic magnetic

TABLE VI

Constitutional formula	A		B	
	(I) 	(II) 	(I) 	(II) 
	$-\chi \times 10^6$	$-\chi \times 10^6$	$-\chi \times 10^6$	$-\chi \times 10^6$
$(\chi_a)_1$	0·2531	0·1954	0·3284	0·3470
$(\chi_m)_1$	32·64	25·26	42·43	44·84
$(\chi_a)_2$	0·2599	0·1866	0·3357	0·3382
$(\chi_m)_2$	33·59	24·11	43·88	43·69
$(\chi_a)_3$	0·2522	0·1949	0·3278	0·3465
$(\chi_m)_3$	32·58	25·191	42·37	44·77
$(\chi_a)_4$	0·2595	0·1861	0·3353	0·3376
$(\chi_m)_4$	33·53	24·042	43·32	43·62
$(\chi_a)_E$	..	..	..	0·3515
$(\chi_m)_E$	..	..	..	45·41
$(\chi_a)O_1$	..	..	..	0·36
$(\chi_m)O_1$	..	..	..	46·51
$(\chi_a)O_2$	..	..	..	0·3948
$(\chi_m)O_2$	..	..	..	51·00
$(\chi_a)O_3$	..	..	..	0·4149
$(\chi_m)O_3$	..	..	..	53·6

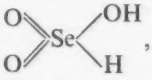
O_1 refers to *Int. Crit. Tables.*

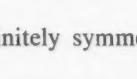
O_2 refers to Rao's values (*loc. cit.*)

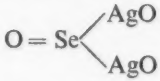
O_3 refers to the value calculated by Kido's data (*Sci. Rep. Tohoku, Imp. Univ.*, 1933, **22**, 835).

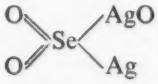
susceptibility of oxygen determined from substances characterised by strong binding is much less diamagnetic than that in compounds of weak binding in which oxygen atoms may exhibit their own magnetic properties without being affected by other atoms in the molecule. Selenious acid is a weak acid and the binding between the oxygen and selenium atoms may be weak. Pauling, Slater and Angus[18] have independently calculated the ionic susceptibility of oxygen atom on theoretical considerations and Angus has shown (*ibid.*) that these values fit in very well with experimental results. These values are $-12{\cdot}6 \times 10^{-6}$ (Pauling), $-13{\cdot}15 \times 10^{-6}$ (Slater) and $-11{\cdot}25 \times 10^{-6}$ (Angus), and are fairly close to each other. Consequently magnetic susceptibility of selenious acid was calculated for the two constitutions using Slater's value for oxygen and the values obtained are given under B of the above Table.

Recently Rao[19] has determined the ionic susceptibility of SeO_3. This value has been utilized also to calculate the magnetic susceptibility of this acid.

It is evident that the values for the constitutional formula (II) are in good agreement with the experimental values showing thereby that selenious acid has the structure  , in the solid state. The values obtained from Kido's and Rao's data are a little higher than the experimental value obtained by the author.

4. *Silver Selenite* (Ag_2SeO_3).—Accepting the unsymmetrical constitution for the selenious acid it is probable that its salts will be also unsymmetrical. To test this point silver selenite (Ag_2SeO_3) was chosen for investigation. But it has been mentioned before that the reaction between ethyl iodide and silver selenite yields symmetrical ethyl selenite (*loc. cit.*) whose constitution has been established further by the action of sodium ethoxide on selenosyl chloride which is definitely symmetrical  . This substance has also been studied in this investigation and its discussion appears in the succeeding paragraphs. Hence silver selenite may have the constitution

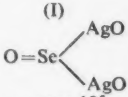
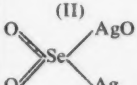
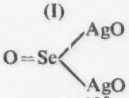
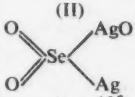
 (I)

or  (II)

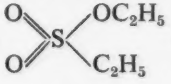
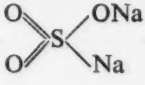
The atomic and molecular susceptibilities for both the forms have been calculated and are compared with the experimental values. The value for AgO is obtained by adding the ionic susceptibilities of Ag ($-31{\cdot}0\times10^{-6}$; *Int. Crit. Tables*) and O ($-4{\cdot}61\times10^{-6}$), since it is of the type R–O–R (Bhatnagar and Mathur, *Physical Principles and Application of Magneto-Chemistry*, p. 90). This comes out to be $-35{\cdot}61\times10^{-6}$. It can be calculated from the magnetic constants of Ag_2O for which χ_a is $-0{\cdot}58\times10^{-6}$ (Bhatnagar and Mathur, *ibid.*, p. 214) and, therefore, χ_m is $-66{\cdot}98\times10^{-6}$. Subtracting the ionic value for Ag ($-31{\cdot}0\times10^{-6}$) the value for AgO comes out to be $-35{\cdot}89\times10^{-6}$, which is nearly the same as obtained by the first method.

In the Table given below the calculated values under A and B are obtained by using, respectively, Pascal's and Slater's value for oxygen. Rao's (*ibid.*) value for SeO_3 ion has been also utilized for these calculations.

TABLE VII

Constitutional formula	A		B	
	(I)  $-\chi \times 10^6$	(II)  $-\chi \times 10^6$	(I)  $-\chi \times 10^6$	(II)  $-\chi \times 10^6$
$(\chi_a)_1$	0·2588	0·2370	0·2874	0·2941
$(\chi_m)_1$	88·78	81·28	98·57	100·86
$(\chi_a)_2$	0·2616	0·2336	0·2901	0·2908
$(\chi_m)_2$	88·73	80·13	99·52	99·75
$(\chi_a)_3$	0·2586	0·2368	0·2872	0·2938
$(\chi_m)_3$	88·72	81·21	98·51	100·84
$(\chi_a)_4$	0·2614	0·2334	0·2900	0·2907
$(\chi_m)_4$	89·67	80·06	99·46	99·692
$(\chi_a)_E$	..	0·298	..	0·298
$(\chi_m)_E$	..	102·2	..	102·2
$(\chi_a)O_1$	..	..	..	0·3117
$(\chi_m)O_1$	..	..	..	106·9
$(\chi_a)O_2$	..	..	..	0·3193
$(\chi_m)O_2$	..	..	..	109·5

O_1 and O_2 refer to the values calculated from Rao's and Kido's data.

It will be seen that the experimental values agree with those calculated for the constitution (II) when Slater's value for oxygen is used. This shows that the constitution of Ag_2SeO_3 is similar to that of selenious acid, that is, Se is hexavalent in the compound and the binding with oxygen atoms is such that only high magnetic value of oxygen is admissible. Also the magnetic data definitely proves that this salt of selenious acid is unsymmetrical. This is in conformity with the constitution of the salts of sulphurous acid such as ethyl ethylsulphonate  and soidum sulphate  .

5. *Selenosyl chloride or selenium oxychloride* ($SeOCl_2$).—There is no indefiniteness regarding the constitution of this compound which is represented as $O=Se\begin{matrix}Cl\\Cl\end{matrix}$ as there is no alternative representation.

The interest in the study of this compound lies in the behaviour of oxygen atom. Using Pascal's value for oxygen ($-3\cdot36\times10^{-6}$) it is found that the theoretically calculated value is much higher than the experimental one. If Slater's value for oxygen ($-13\cdot35\times10^{-6}$) is used, this value is still higher. Stoner[9] (*Magnetism and Matter*, p. 473) and Bhatnagar and Mathur (*loc. cit.*) have shown that if there is only one oxygen atom in a molecule connected by double bond to other atoms, the oxygen atom will be paramagnetic ($+1\cdot8\times10^{-6}$). If this value is used, the calculated results are in better agreement with the experimental ones. But still there is a large discrepancy between the two, which may be due to the absorption of moisture by $SeOCl_2$ and its consequent decomposition into selenium dioxide and hydrochloric acid before it is introduced into the specimen tube. Even with the best care taken to transfer the liquid into the specimen tube as quickly as possible, an observation could only be taken once. For the second observation with the same filling it was found that an increase in weight of the substance had taken place, evidently due to the absorbed moisture. The results obtained are shown below:

TABLE VIII

Constitution $O=Se\begin{matrix}Cl\\Cl\end{matrix}$	χ_a and χ_m obtained by using Pascal's value of O ($-3\cdot35\times10^{-6}$)	χ_a and χ_m obtained by using the value of O = ($+1\cdot8\times10^{-6}$)
$(\chi_a)_1$	$-0\cdot3730\times10^{-6}$	$-0\cdot3419\times10^{-6}$
$(\chi_m)_1$	$-61\cdot96\times10^{-6}$	$-56\cdot8\times10^{-6}$
$(\chi_a)_2$	$-0\cdot3787\times10^{-6}$	$-0\cdot3477\times10^{-6}$
$(\chi_m)_2$	$-62\cdot91\times10^{-6}$	$-57\cdot75\times10^{-6}$
$(\chi_a)_3$	$-0\cdot3727\times10^{-6}$	$-0\cdot3416\times10^{-6}$
$(\chi_m)_3$	$-61\cdot90\times10^{-6}$	$-56\cdot74\times10^{-6}$
$(\chi_a)_4$	$-0\cdot3784\times10^{-6}$	$-0\cdot3473\times10^{-6}$
$(\chi_m)_4$	$-62\cdot85\times10^{-6}$	$-57\cdot69\times10^{-6}$
$(\chi_a)_5$	..	$-0\cdot2929\times10^{-6}$
$(\chi_m)_5$	..	$-48\cdot65\times10^{-6}$

TABLE IX

Selenium Compounds

Compound	Constitution	$-\chi_a \times 10^6$ and $-\chi_m \times 10^6$ observed by the authors		$-\chi_a \times 10^6$ and $-\chi_m \times 10^6$ calculated by Slater's method	$-\chi_a \times 10^6$ and $-\chi_m \times 10^6$ calculated by the modification of Slater's method	$-\chi_a \times 10^6$ and $-\chi_m \times 10^6$ calculated by by Angus's method	$-\chi_a \times 10^6$ and $-\chi_m \times 10^6$ calculated by the modification of Angus's method
Se_2Br_2 ..	Br–Se–Se–Br	(χ_a) 0·3544		0·3479	0·3674	0·3400	0·3636
		(χ_m) 112·6		110·72	119·64	108·18	115·68
Se_2Cl_2 ..	Cl–Se–Se–Cl	(χ_a) 0·4134		0·3930	0·4319	0·3819	0·4145
		(χ^m) 94·79		90·12	99·04	87·58	95·04
H_2SeO_3 ..		(χ_a) 0·3515	0·36	0·3470	0·3382	0·3465	0·3376
		(χ_m) 45·41	46·51 (*Int. Crit. Tab.*)	44·84	43·69	44·77	43·62
Ag_2SeO_3 ..		(χ_a) 0·298		0·2941	0·2908	0·2938	0·2937
		(χ_m) 102·2		100·86	99·75	100·841	99·692
SeO Cl_2 ..		(χ_a) 0·2929		0·3419	0·3477	0·3416	0·3473
		(χ_m) 48·65		56·8	57·75	56·74	57·69

It is probable that the strong binding between the oxygen and selenium atoms has the effect of reducing the diamagnetism to a greater extent than that shown by the paramagnetic value. The discrepancy in the theoretical and the experimental values observed in the case of $SeOCl_2$ is also exhibited by thionyl chloride (to be discussed in a paper to be published soon) which is analogous to it.

Table IX gives the correct constitution of various compounds of Se investigated along with the experimental and calculated values observed by the author. It will be seen that in all calculations made in this investigation Slater's and Angus's values have been found to give much satisfactory results. It may also be remarked that the choice of the value for O is an important one and depends upon the type of binding in the molecule.

The authors welcome this opportunity of recording their thanks to Dr. S. S. Bhatnagar, O.B.E., D.Sc., for his helpful suggestions and criticisms.

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ON A LINEAR DIOPHANTINE EQUATION

By S. S. Pillai

Received April 25, 1940
(Communicated by Prof. B. S. Madhava Rao)

Let $d_r = (a_1, a_2, \ldots, a_{r-1}, a_{r+1}, \ldots a_n)$, $r = 1, 2, \ldots, n$;

$D = d_1 d_2 \ldots d_n$

and $m_r = a_r d_r / D$, $r = 1, 2, \ldots, n$.

$F = F(a_1, a_2, \ldots, a_n)$ is the least value (if any) of

$$|X_1| + |X_2| + \cdots + |X_n|$$

satisfying the Diophantine equation

$$a_1 X_1 + a_2 X_2 + \ldots + a_n X_n = 1. \tag{1}$$

The object of this note is to prove

Theorem: If $(a_1, a_2, \ldots, a_n) = 1$, then the equation (1) is solvable for $X_1, \ldots, X_n$ in terms of integers, and

$$F \leqslant d_1 + d_2 + \ldots + d_{n-2} + m_n d_{n-1} + m_{n-1} d_n - n + 1,$$

where the suffixes are so chosen that

$$m_1 \leqslant m_2 \leqslant \ldots \leqslant m_{n-3} \leqslant m_{n-2} \leqslant m_{n-1} \cdot m_n. \tag{2}$$

Lemma: If $\alpha = |A|$, $\beta = |B|$, $(A, B) = 1$ and $1 \leqslant C \leqslant \alpha\beta$, then we can find x and y such that

$$Ax + By = C;\ 0 \leqslant |x| \leqslant \beta - 1;\ \text{and } 1 \leqslant |y| \leqslant \alpha.$$

Consider the sets

$$\left.\begin{array}{ll} \beta y - \alpha x, & x = 0, 1, \ldots, [\beta y/\alpha]; \\ \beta y + \alpha X, & X = 1, 2, \ldots, [(\alpha\beta - \beta y)/\alpha]; \\ \text{where} & y = 1, 2, \ldots, \alpha. \end{array}\right\} \tag{3}$$

Since $[\beta y/\alpha] + 1 + [(\alpha\beta - \beta y)/\alpha] = \beta$, when $y \neq \alpha$,

and $= \beta + 1$, when $y = \alpha$, it follows that there are $\alpha\beta + 1$ numbers in the above sets. (4)

Further, all these numbers $\leqslant \alpha\beta$ and $\geqslant 0$. (5)

Again, if $\beta y - \alpha x = \beta y_1 - \alpha x_1$ or $\beta y_1 + \alpha X_1$,

or $\beta y + \alpha X = \beta y_1 + \alpha X_1$,

where x_1, y_1, X_1 satisfy the conditions imposed on x, y, X respectively and $y \neq y_1$, then (6)

$$\beta(y-y_1) = \alpha(x-x_1),\ \alpha(x+X_1) \text{ or } \alpha(X_1-X).$$

Since $y \neq y_1$ and $(\alpha, \beta) = 1$, we get that $y-y_1$ is a multiple of α and hence

$$|y-y_1| \geqslant \alpha.$$

But from (3) and (6), $\quad |y-y_1| \leqslant \alpha - 1.$

Hence, under the restrictions, the above equations are impossible, and consequently all the above $\alpha\beta+1$ numbers are different.

From this and (5), we get that there are x, y such that

$$\alpha x + \beta y = C,\ |x| \leqslant \beta - 1 \text{ and } 1 \leqslant |y| \leqslant \alpha,$$

provided that $\quad 1 \leqslant C \leqslant \alpha\beta.$

By adjusting properly the signs of x, y in the above, we get the lemma.

Now we can prove the theorem.

Since $(a_1, a_2, \ldots, a_n) = 1$, $d_1, d_2, \ldots, d_n$ are all prime to each other and hence m_r is an integer with $(m_r, d_r) = 1$.

From this and the lemma, it follows that the following equations are solvable in terms of $X_1, \ldots, X_n$ and $Y_1, \ldots, Y_{n-2}$ with the restrictions specified;

(1) $\dfrac{m_1 D}{d_1} \cdot X_1 + d_1 Y_1 = 1;\ |X_1| < d_1, |Y_1| \leqslant m_1 D/d_1;$

(2) $\dfrac{m_2 D}{d_1 d_2} \cdot X_2 + d_2 Y_2 = Y_1;\ |X_2| < d_2, |Y_2| \leqslant \dfrac{m_2 D}{d_1 d_2};$

(3) $\dfrac{m_3 D}{d_1 d_2 d_3} \cdot X_3 + d_3 Y_3 = Y_2;\ |X_3| < d_3, |Y_3| \leqslant \dfrac{m_3 D}{d_1 d_2 d_3};$

. . . . . .

. . . . . .

$(n-2)$ $m_{n-2} d_{n-1} d_n X_{n-2} + d_{n-2} Y_{n-2} = Y_{n-3},\ |X_{n-2}| < d_{n-2}, |Y_{n-2}| \leqslant m_{n-2} d_{n-1} d_n;$

$(n-1)$ $m_{n-1} d_n X_{n-1} + m_n d_{n-1} X_n = Y_{n-2},\ |X_{n-1}| < m_n d_{n-1}, |X_n| \leqslant m_{n-1} d_n.$

In the above, equation (1) is solved first. In virtue of (2), the second equation is solvable, then the second is solved, and so on. Now multiply the second equation by d_1; the third by $d_1 d_2 \ldots$; $(n-2)$th by $d_1 d_2 \ldots d_{n-3}$;

and $(n-1)$th by $d_1 d_2 \ldots d_{n-2}$; and add all. Then we get

$$D(m_1 X_1/d_1 + m_2 X_2/d_2 + \ldots + m_n X_n/d_n) = 1.$$

i.e.,
$$a_1 X_1 + a_2 X_2 + \ldots + a_n X_n = 1.$$

Further $|X_1| < d_1; \ldots; |X_{n-2}| < d_{n-2}; |X_{n-1}| < m_n d_{n-1}; |X_n| \leqslant m_{n-1} d_n.$

From these, the theorem follows immediately.

In one of my previous papers, the theorem was announced in a form which was obviously wrong.

ON WARING'S PROBLEM WITH POWERS OF PRIMES

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Received April 25, 1940

(Communicated by Prof. B. S. Madhava Rao)

Let p^θ be the highest power of the prime p which divides the integer k, and let

$$\gamma = \begin{cases} \theta + 2 \text{ for } p = 2,\ 2/k \\ \theta + 1 \text{ otherwise.} \end{cases}$$

$K = p_1^{\gamma_1} \ldots p_n^{\gamma_n}$, where $p_1, \ldots, p_n$ are primes for which $(p_r - 1)/k$,

$$r = 1, 2, \ldots, n.$$

$d_r = p_r^{\gamma_r}$.

Hereafter p stands for a prime which divides K, and P denotes the smallest prime which does not divide K.

$t = t(k)$ is the least value of s such that the congruence

$$N \equiv x_1 + x_2 + \ldots + x_s \pmod{K}$$

is solvable for every N in terms of x, where $x = 0$, p^k, or P^k.

$$D_s = d_{s+1} \ldots d_n; \quad Q_s = d_1 \ldots d_s.$$

$$T_0 = 2(d_1 + d_2 + \ldots + d_s - s) + D_s - 1.$$

In a previous issue of these *Proceedings*,* I proved that

$$t(k) \leqslant 3(d_1 + \ldots + d_{n-1}) + 2^\gamma - 2n + 2.$$

The object of this note is to prove

THEOREM: $$t(k) \leqslant T_0.$$

Though the improvement is slight, the proof is easier. The function $t(k)$ plays some part in the problem given in the title.

Lemma 1: $p_r^k \equiv h_r \cdot \dfrac{K}{d_r} + 1 \pmod{K}$, where $(h_r, d_r) = 1$.

This follows from Fermat's theorem.

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* Section A, 1939, Vol. 9, No. 1, pp. 29–34.

Lemma 2: When $1 \leqslant a_r \leqslant d_r$, $r = 1, \ldots, s$,

$h_1 a_1 d_2 \ldots d_s + h_2 a_2 d_1 d_3 \ldots d_s + \ldots + h_s a_s d_1 \ldots d_{s-1}$ runs through a complete residue system (mod. Q_s).

In order to prove the result, it is enough if we show that for no two different sets $a_1, a_2, \ldots, a_s$, the expression belongs to the same residue class (mod. Q_s).

If possible, when $1 \leqslant a_r \leqslant d_r$, $1 \leqslant A_r \leqslant d_r$, where at least for one r,

$$a_r \neq A_r, \text{ let}$$

$$h_1 a_1 d_2 \ldots d_s + \ldots + h_s a_s d_1 \ldots d_{s-1} \equiv h_1 A_1 d_2 \ldots d_s + \ldots + h_s A_s d_1 \ldots d_{s-1} \pmod{Q_s}.$$

Then $h_r d_1 \ldots d_{r-1} d_{r+1} \ldots d_s (A_r - a_r) + M d_r \equiv 0 \pmod{Q_s}$.

So from lemma (1), $A_r - a_r \equiv 0 \pmod{d_r}$, $r = 1, \ldots, s$.

Hence the lemma is proved.

Lemma 3: When $1 \leqslant a_r \leqslant d_r$, $r = 1, \ldots, s$,

$\Sigma p_r^k \cdot a_r \equiv \Sigma a_r + M \cdot D_s \pmod{K}$, where M runs from 1 to Q_s.

Now, $\Sigma p_r^k \cdot a_r \equiv \Sigma (1 + h_r \cdot K/d_r) a_r \pmod{K}$, from lemma (1).

$$= \Sigma a_r + \Sigma (h_r a_r K/d_r) = \Sigma a_r + \frac{K}{Q_s} \{h_1 a_1 d_2 \ldots d_s + \ldots + h_s a_s d_1 \ldots d_{s-1}\}$$

$$\equiv \Sigma a_r + M \cdot D_s \pmod{K}.$$

From lemma (2), we get that M runs from 1 to Q_s.

Now we are in a position to prove our theorem.

†Let $B_M \equiv \sum_{r=1}^{s} a_r + M \cdot D_s \pmod{K}$, where $1 \leqslant B_M \leqslant K$.

Now $B_M \leqslant (d_1 + \ldots + d_s) + M \cdot D_s$ and $B_M \geqslant s + M \cdot D_s$.

So if $B_{M+1} \geqslant B_M$, then $B_{M+1} - B_M \leqslant D_s + d_1 + \ldots + d_s - s$,

and if $B_{M+1} \leqslant B_M$, then $B_M - B_{M+1} \leqslant d_1 + \ldots + d_s - s - D_s$.

Hence if $A_1, A_2, \ldots A_u$ are the $B_1, B_2, \ldots B_{Q_s}$ arranged in increasing order, and $A_{u+1} = K + A_1$, then

$$A_{m+1} - A_m \leqslant D_s + d_1 + \ldots + d_s - s. \qquad (1)$$

---

† First $a_1, \ldots, a_s$ are given values satisfying the conditions $1 \leqslant a_r \leqslant d_r$, $r = 1, \ldots, s$; then M becomes definite as it is a function of $a_1 \ldots, a_s$. So B_M is a function of $a_1, a_2, \ldots, a_s$.

Given N, we can find one S and t such that

$$N \equiv S \text{ (mod. K)}, \text{ and } A_t \leqslant S < A_{t+1}, \text{ where } 1 \leqslant t \leqslant u.$$

Hence,
$$N \equiv A_t + S - A_t \text{ (mod. K)},$$

$$\equiv \sum_{r=1}^{s} a_r \cdot p_r^k + (S - A_t) \cdot P^k \text{ (mod. K)}.$$

Therefore, $t(k) \leqslant \Sigma a_r + S - A_t \leqslant \Sigma d_r + A_{t+1} - A_t - 1 \leqslant T_0$, from (1)

A THEOREM ON NORMAL RECTILINEAR CONGRUENCES

By Ram Behari
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Received June 10, 1940

Abstract

1. Let a rectilinear congruence be defined by

$$\xi = x + tX, \eta = y + tY, \zeta = z + tZ,$$

where x, y, z, X, Y, Z are functions of two variables u and v.

Denoting Sannia's two quadratic forms[1]

$$Edu^2 + 2\,Fdudv + Gdv^2 \text{ and } \delta du^2 + 2\,\delta' dudv + \delta'' dv^2,$$

by f and ϕ respectively, we know that the equations of (*i*) the surfaces whose spherical representations are minimal lines, (*ii*) developable surfaces, and (*iii*) surfaces of distribution,[2] are respectively

$$f = 0,\ \phi = 0,\ J(f, \phi) = 0.^3$$

The object of this paper is to obtain analytically a property of the spherical representations of the distributive ruled surfaces through a line of a normal rectilinear congruence.

2. When the congruence is normal, the focal planes are at right angles and hence the two quadratic forms f and ϕ are harmonic, so that

$$E\delta'' + G\delta - 2\,F\delta' = 0.$$

This relation can also be written in the form $f - f' = 0$ where f stands for $\Sigma X_1 x_2$ and f' for $\Sigma X_2 x_1$, the subscripts 1 and 2 denoting differentiation with regard to u and v respectively.

We have

$$\frac{1}{\sqrt{EG - F^2}}\left(\frac{\delta\gamma'}{\delta u} - \frac{\delta\gamma}{\delta v}\right) = \frac{2\,F\delta' - E\delta'' - G\delta^4}{EG - F^2}, \tag{1}$$

where $\gamma\ (\equiv \Sigma X x_1)$ and $\gamma'\ (\equiv \Sigma X x_2)$ are given by

$$-\gamma_1\sqrt{EG - F^2} = \delta_2 - \delta_1' - \Gamma''\delta + (\Gamma - \Delta')\,\delta' + \Delta\delta'' \tag{2}$$

and

$$\gamma_1'\sqrt{EG - F^2} = \delta_1'' - \delta_2' + \Gamma''\delta + (\Delta'' - \Gamma')\,\delta' - \Delta'\delta'' \tag{3}$$

where the letters Γ, Γ'', Γ''; Δ, Δ', Δ'' have their usual meanings.[5]

Let the curves on the sphere which represent the surfaces of distribution be taken as the parametric curves, then

$$J(f, \phi) \equiv \begin{vmatrix} Edu + Fdv & Fdu + Gdv \\ \delta du + \delta' dv & \delta' du + \delta'' dv \end{vmatrix} = 0$$

must be the same as $dudv = 0$, and therefore we have

$$\delta' = 0, \ F = 0. \tag{4}$$

Also since the congruence is normal, we have

$$\frac{\delta\gamma'}{\delta u} - \frac{\delta\gamma}{\delta v} = 0; \ 2F\delta' - E\delta'' - G\delta = 0 \tag{5}$$

so that (1) is satisfied identically, and (2), (3), (5) become, making use of (4),

$$\delta_2 - \Gamma'\delta + \Delta\delta'' = 0 \tag{6}$$

$$\delta_1'' + \Gamma''\delta - \Delta'\delta'' = 0 \tag{7}$$

$$E\delta'' + G\delta = 0 \tag{8}$$

But $\Gamma' \equiv \dfrac{GE_2 - FG_1}{2(EG - F^2)} = \dfrac{E_2}{2E}$; $\Delta \equiv \dfrac{-FE_1 - EE_2 + 2EF_1}{2(EG - F^2)} = -\dfrac{E_2}{2G}$;

$$\Gamma'' \equiv \frac{-FG_2 - GG_1 + 2GF_2}{2(EG - F^2)} = -\frac{G_1}{2E}; \ \Delta' \equiv \frac{EG_1 - FE_2}{2(EG - F^2)} = \frac{G_1}{2G};$$

$\therefore$ (6) reduces to $\quad \delta_2 - \left(\dfrac{\delta}{E} + \dfrac{\delta''}{G}\right) \cdot \dfrac{E_2}{2} = 0,$

and (7) reduces to $\quad \delta_1'' - \left(\dfrac{\delta}{E} + \dfrac{\delta''}{G}\right) \cdot \dfrac{G_1}{2} = 0.$

$\therefore \quad \delta_2 = 0$ and $\delta_1'' = 0$ from (8).

Hence δ is a function of u only and δ'' is a function of v only. But

$$\frac{\delta}{\delta''} = -\frac{E}{G} \text{ from (8).}$$

$$\therefore \quad \frac{E}{G} = \frac{\text{a function of } u \text{ only}}{\text{a function of } v \text{ only}}$$

$\therefore \quad \dfrac{\delta^2}{\delta u \delta v} \log\left(\dfrac{E}{G}\right) = 0$, which shows that the parametric curves are isometric.

Hence we get the theorem:

The curves on the sphere representing the distributive ruled surfaces through a line of a normal rectilinear congruence are isometric.

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THE YOUNG'S MODULUS OF DIAMOND

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(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

Introduction

The only elastic property of diamond which has been experimentally studied up to this time is its bulk modulus, the value of which as determined by Adams[1] and Williamson[2] are respectively $6{\cdot}25\times10^{12}$ and $5{\cdot}56\times10^{12}$ dynes per sq. cm. In the present note an account of an experimental determination of the Young's modulus of diamond for a rod, whose axis is nearly parallel to the octahedral cleavage of the crystal is given.

The Young's modulus E for any cubic crystal along a direction whose direction cosines are l, m, n with respect to the crystallographic axes, is given by[3]

$$\frac{1}{E}=\frac{c_{12}}{(c_{11}-c_{12})(c_{11}+2c_{12})}-\frac{1}{2c_{44}}-\left(\frac{1}{c_{11}-c_{12}}-\frac{1}{2c_{44}}\right)(l^4+m^4+n^4),$$

where c_{11}, c_{12}, c_{44} are the three elastic constants. The surface described by a radius vector of magnitude 1/E and direction cosines l, m, n, gives a picture of the variation of the Young's modulus with direction. It can be easily shown that for any direction lying in the octahedral plane of any cubic crystal.

$$l^4+m^4+n^4=\tfrac{1}{2}.$$

Hence the section of the elastic surface by the (111) plane is a circle. Its radius is equal to the reciprocal of the Young's modulus along the diagonal of a face of the cube, for, the direction cosines of this diagonal are

$$l=\frac{1}{\sqrt{2}},\quad m=\frac{1}{\sqrt{2}},\quad \text{and}\quad n=0,$$

thus making

$$l^4+m^4+n^4=\tfrac{1}{2}.$$

Thus all rods cut *with their lengths parallel to this plane*, have the same Young's modulus.

The rod used in the present determination has its axis inclined at an angle of about 1° to the (111) plane as found by an X-ray examination of

the specimen carried out by Dr. P. Nilakantan. But the broad faces of the rectangular specimen make considerable angles (13° and 16°) with the (111) plane. The Young's modulus was determined by bending the rod, the neutral surface being parallel to the broad faces. Since during bending the elongations and contractions of the various filaments take place in a direction parallel to the axis of the rod, *i.e.*, in a direction practically parallel to the (111) plane, the Young's modulus determined is the one along this plane.

For a direction normal to the (111) plane, the values of the direction cosines are

$$l = m = n = \frac{1}{\sqrt{3}},$$

which makes the value of E greater than that in a direction lying in the octahedral plane. For a direction along the cubic axis,

$$l = 1, \text{ and } m = n = 0,$$

which makes the value of E smaller than that in a direction lying in the octahedral plane. So the value obtained in this determination will be between the maximum and minimum values.

2. *Method*

The principle of the method employed is the same as that of the ' Scale and Telescope method' of Voigt.[4] But to ensure greater accuracy, the scale was replaced by a fine narrow illuminated slit and the telescope by a long focus camera,—the shift of the image being registered photographically.

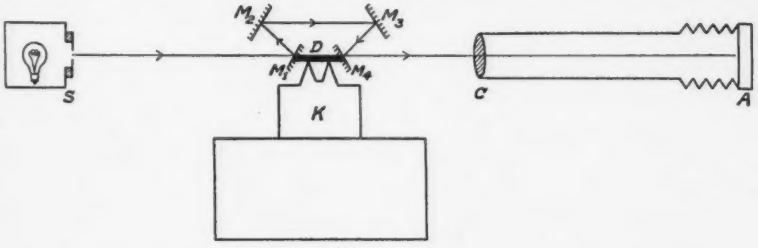

FIG. 1

The specimen D was supported horizontally on two parallel knife edges 0·393 cm. apart, cut out on a block of tool steel which was tempered after working the knife edges. The bottom of the block was ground plane and made to sit perfectly on the plane surface of a heavy iron anvil.

Two cover glass slips $\mathbf{M}_1$ and $\mathbf{M}_4$ of good optical quality were selected by observation of the Haidinger's rings given by them and silvered by the evaporation process. The mirrors were fixed to the ends of the specimen

rigidly by pitch. $\mathbf{M}_2$ and $\mathbf{M}_3$ were two other fixed mirrors also of good optical quality. S was a narrow slit illuminated by a 100 watt lamp. **CA** was the long focus camera of which the lens **C** was the achromatic objective of a one metre telescope.

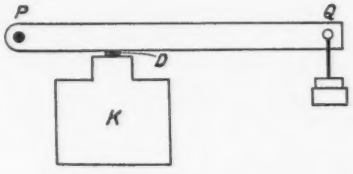

FIG. 2

Fig. 2 illustrates the method of applying the load on the specimen. PQ was a rigid steel lever pivoted about a smooth horizontal axle passing through P, the length of the lever being at right angles to the length of the specimen D. That part of the lever, which rested on D, was ground into a fine knife edge. The load was applied at Q, thus producing a magnified vertical force on D.

The image of the slit after successive reflections at the mirrors $\mathbf{M}_1$, $\mathbf{M}_2$, $\mathbf{M}_3$ and $\mathbf{M}_4$ was focussed by the camera lens **C** on the photographic plate **A**. The positions of the image before and after loading the specimen were recorded photographically on the same plate. The shift of the image was measured accurately using a Hilger micrometer reading to thousandths of a millimetre.

3. *Theory*

If θ be the angular tilt of each of the two mirrors $\mathbf{M}_1$ and $\mathbf{M}_4$ produced by the bending of the specimen due to an effective central load of W, we have

$$\theta = \frac{\mathrm{W}\, l^2}{16\, \mathrm{E}\, \mathrm{I}},$$

where l is the distance between the knife edges, E is the Young's modulus and I is the moment of inertia of the cross-section about the neutral surface.

If s be the shift of the image on the photographic plate whose distance from the optic centre of the lens is **C A**, the angle ϕ through which the final ray is turned is given by $s/\mathbf{C}\,\mathbf{A}$. Denoting the distance of $\mathbf{M}_1$ from the slit by **D**, the distance $\mathbf{M}_1\,\mathbf{M}_2$ by a, the distance $\mathbf{M}_2\,\mathbf{M}_3$ by b, the distance $\mathbf{M}_3\,\mathbf{M}_4$ by c, and the distance $\mathbf{M}_4\,\mathbf{C}$ by d, we have

$$\phi\,(\mathbf{D}+a+b+c+d) = \{4\,\mathbf{D}+2\,(a+b+c)\}\,\theta.$$

4. Measurements

As mentioned before, the distance between the knife edges was 0·393 cm. The moment of inertia of area of cross-section, *i.e.*, the value of I for the specimen was 0·0000273 cm.[4] In the experiment the distance **C A** was 150·1 cm. and the distance **D** was 245 cm. The mean shift on the photographic plate, for an effective load of 1,765 gm. on the specimen was 0·0484 cm.

The value of the Young's modulus calculated from the mean shift is $5{\cdot}5 \times 10^{12}$ dynes per sq. cm. The accuracy claimed is only 1%.

The author is highly thankful to Sir C. V. Raman, Kt., F.R.S., N.L., for the loan of the diamond and for the valuable suggestions and guidance throughout the work. The author wishes to thank Dr. Nilakantan for kindly determining the orientation of the (111) planes in the specimen.

5. Summary

It is shown that the section of the elastic surface of a cubic crystal by an octahedral plane is a circle. Voigt's 'scale and telescope' method for the Young's modulus determinations of crystals is improved by the use of a narrow slit and a long focus camera, the shift being recorded photographically and measured by a Hilger micrometer. The experimental value for the Young's modulus of diamond in any direction lying in the octahedral plane is found to be $5{\cdot}5 \times 10^{12}$ dynes/cm.^{2} The maximum value of the Young's modulus of a cubic crystal being in a direction normal to this plane, we can expect a higher value for a rod cut normal to the octahedral plane.

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MOLECULAR STRUCTURE OF SOME TELLURIUM COMPOUNDS DETERMINED BY MAGNETIC METHOD

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(Communicated by Dr. Mata Prasad, D.Sc., F.I.C., F.A.Sc.)

The structures of some of the selenium compounds obtained by the use of the Langevin equation and Slater's and Angus's methods for the calculation of $\Sigma \bar{r}^2$ are given in the previous paper.[1] In this investigation an attempt has been made to discuss the constitution of some tellurium compounds. Tellurium belongs to the same group of elements as S and Se and the constitution of their compounds may throw light on the constitution of the compounds of tellurium. The Guoy balance and the method of working described in the previous paper were used in this investigation. The magnetic susceptibilities of the compounds investigated are given in Table I.

Table I

Substance	Molecular formula	$\chi_a \times 10^6$	$\chi_m \times 10^6$
Tellurious acid	H_2TeO_3	−0·1965	− 34·89
Tellurium dichloride	$TeCl_2$	−0·4760	− 94·45
Tellurium dibromide	$TeBr_2$	−0 3701	−106·20
Telluric acid	H_2TeO_4, $2H_2O$	−0·2508	− 57·55
Dimethyl tellurium diiodide	$(CH_3)_2TeI_2$	−0·3535	−145·40
Dimethyl tellurium dichloride	$(CH_3)_2TeCl_2$	−0·4047	− 92·43

All substances except dimethyl tellurium diiodide and dimethyl tellurium dichloride were obtained either from Kahlbaum or from Theoder Schuchardt and were of extra pure quality. The author is thankful to Miss K. D. Gavankar, M.Sc., Analyst, Royal Institute of Science, for preparing the two substances in this laboratory.

Dimethyl tellurium diiodide $(CH_3)_2TeI_2$.—Amorphous tellurium (25 g.) and methyl iodide (55 g.) were kept in a hard glass bulb on a water-bath

[1] *Proc. Ind. Acad. Sci.*, (A), 1940, **12**, 185.

at 80° for about 48 hours. It was then cooled and the substance was extracted with chloroform from which it was obtained as red crystals,[2] m.p. = 125°–26°; standard value 127°. The density of the crystals was found to be 2·651. gm./c.c.

Dimethyl tellurium dichloride $(CH_3)_2TeCl_2$.—To dimethyl tellurium diiodide (about 5 g.) concentrated aqueous ammonia was added drop by drop till the red salt was transformed entirely into a pasty greyish white mass. The precipitate was dissolved in water with one or two drops of ammonia and an aqueous solution [50 c.c. of the solution containing 12·14 g. of $AgNO_3$ and just sufficient quantity of NH_4OH to redissolve the precipitate of Ag(OH)] was added to it. The mixture was boiled and filtered and the filtrate was evaporated till no smell of ammonia was detected. Then it was diluted and any silver iodide present was removed. The excess of silver nitrate was removed by the repeated addition of HBr. The remaining solution was evaporated to about 100 c.c. and was treated with HCl until no further precipitation took place. The dichloride thus obtained was purified by crystallisation from alcohol (m.p. = 93°–94°; literature = 92°).

Discussion of Results

The values of $\Sigma \bar{r}^2$ and the ionic susceptibilities for Te in various valency states, calculated according to Slater's and Angus's methods as well as with the slight changes mentioned in the previous paper, are given in Table II.

TABLE II

Diamagnetic susceptibilities of Te *in various valency states calculated from various methods*

Valency states	$\Sigma \bar{r}^2$ calculated by Slater's method	$\chi \times 10^6$ calculated by Slater's method	$\Sigma \bar{r}^2$ calculated by modification in Slater's method	$\chi \times 10^6$ calculated by modification in Slater's method using constant 0·790 instead of 0·807	$\Sigma \bar{r}^2$ calculated by Angus's method	$\chi \times 10^6$ calculated by Angus's method	$\Sigma \bar{r}^2$ calculated by modification in Angus's method	$\chi \times 10^6$ calculated by modification in Angus's method and using constant 0·790 instead of 0·807
Te divalent ..	66·19	−53·43	45·66	−36·08	66·36	−53·30	56·08	−44·30
Te tetravalent	39·01	−31·49	30·28	−23·92	38·85	−31·35	30·10	−23·78
Te hexavalent	22·08	−17·81	19·71	−15·57	21·92	−17·69	19·53	−15·43

These values were employed to calculate the magnetic susceptibilities and have been designated with the same symbols as given in the previous paper (*loc. cit.*).

[2] *Jour. Chem. Soc.*, 1920, **86**, 117.

Tellurious Acid (H_2TeO_3).—Like sulphurous and selenious acids there are two possibilities for its constitution: $O=Te(OH)(OH)$ (I) and $O_2Te(OH)H$ (II). The experimental and calculated values for tellurious acid, on the basis of Pascal's value for O ($-3\cdot36\times10^{-6}$), are given under A of the Table III.

TABLE III

Constitution	A		B	
	Symmetrical $O=Te(OH)(OH)$ $-\chi\times10^6$ (I)	Unsymmetrical $O_2Te(OH)H$ $-\chi\times10^6$ (II)	Symmetrical $O=Te(OH)(OH)$ $-\chi\times10^6$ (I)	Unsymmetrical $O_2Te(OH)H$ $-\chi\times10^6$ (II)
$(\chi_a)_1$	0·2813	0·1978	0·3364	0·3089
$(\chi_m)_1$	49·93	35·12	59·72	54·70
$(\chi_a)_2$	0·2386	0·1852	0·2938	0·2955
$(\chi_m)_2$	42·36	32·88	52·15	52·46
$(\chi_a)_3$	0·2805	0·1972	0·3357	0·3075
$(\chi_m)_3$	49·79	35·00	59·58	54·58
$(\chi_a)_4$	0·2373	0·1844	0·2930	0·2947
$(\chi_m)_4$	42·12	32·74	52·01	52·32
$(\chi_a)_E$	..	0·1966	..	..
$(\chi_m)_E$	..	34·89	..	..
$(\chi_a)_{O_1}$	..	0·1900	..	..
$(\chi_m)_{O_1}$	..	33·72	..	..
$(\chi_a)_{O_2}$	..	0·2027	..	..
$(\chi_m)_{O_2}$	..	35·97	..	..
$(\chi_a)_{O_3}$	..	0·1897	..	..
$(\chi_m)_{O_3}$	..	33·68	..	..

O_1 Refers to the values obtained by S. Meyer (Mellor's *Inorganic Chemistry*, **11**, 73).

O_2 Refers to the values calculated from Bragg's data by Bhatnagar and Luther (*J. Ind. Chem. Soc.*, 1929, **3**, 30).

O_3 Refers to values calculated as an electronic isomer by Bhatnagar and Dhawan, also by Bhatnagar and Mathur (*Phil. Mag.*, 1928, **5**, 536 ; 1928, **6**, 217).

The calculated values for the constitution II agree well with the experimental values thus confirming that the constitution $O_2Te(OH)H$ for the tellurious acid is similar to that of the selenious acid. This is to be expected from the similarity in the behaviour of selenium and tellurium and their

compounds. It should, however, be noted that in the calculation of the molecular susceptibilities of selenious acid Slater's value for O ($-13{\cdot}15\times10^{-6}$) was used. Calculations made with this value in the case of tellurious acid are shown under B of the above table. No value thus calculated agrees with the experimental value showing thereby that Pascal's value alone can be employed in this case. The reason for this peculiarity may be found in the fact that the binding between oxygen and tellurium may be stronger than that between oxygen and selenium, for, lower diamagnetic value of oxygen is admissible in the calculation of the susceptibility of tellurious acid.

International Critical Tables give for tellurious acid $\chi_a = -0{\cdot}24\times10^{-6}$ or $\chi_m = -42{\cdot}60\times10^{-6}$. These values agree neither with the calculated ones nor with those experimentally found by the author and other workers and need correction.

Tellurium dichloride ($TeCl_2$).—Tellurium does not form monochloride of the type Te_2Cl_2. This behaviour is unlike selenium and sulphur which yield compounds of the type Se_2Cl_2 and S_2Cl_2. Therefore dichloride was chosen for investigation. This compound is very unstable and the decomposition begins even when the tube is being filled up. Hence great precautions were taken to fill the tube and the observations were taken as quickly as possible. The results obtained experimentally and those calculated for the constitution $Te\begin{smallmatrix}Cl\\Cl\end{smallmatrix}$ are given below:

TABLE IV

Constitution	$Te\begin{smallmatrix}Cl\\Cl\end{smallmatrix}$ $-\chi\times10^6$
$(\chi_a)_1$	0·4928
$(\chi_m)_1$	97·83
$(\chi_a)_2$	0·4057
$(\chi_m)_2$	80·48
$(\chi_a)_3$	0·4925
$(\chi_m)_3$	97·70
$(\chi_a)_4$	0·4471
$(\chi_m)_4$	88·70
$(\chi_a)_E$	0·4760
$(\chi_m)_E$	94·45

The calculated values are slightly different from the experimental ones, but in view of the experimental difficulties mentioned above, the results obtained may be taken to be in good agreement with the theory.

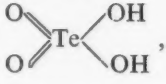
Tellurium dibromide ($TeBr_2$).—This compound also, like $TeCl_2$, is an unstable one. With all the necessary care taken in the measurement it cannot be said that the experimental value is the susceptibility of the pure compound.

TABLE V

Constitution	$Te\langle^{Br}_{Br}$ $-\chi \times 10^6$
$(\chi_a)_1$	0·4121
$(\chi_m)_1$	118·43
$(\chi_a)_2$	0·3515
$(\chi_m)_2$	101·08
$(\chi_a)_3$	0·4117
$(\chi_m)_3$	118·30
$(\chi_a)_4$	0·3804
$(\chi_m)_4$	109·30
$(\chi_a)_E$	0·3701
$(\chi_m)_E$	106·20

The observed discrepancy between the calculated and the experimental values may be due to the unstable nature of the compound. In both the dichlorides and dibromides, the divalent tellurium tends to undergo self-oxidation and reduction, forming a solid solution of the element in the tetrachloride and tetrabromide.[3] Further both of them are hygroscopic and the water absorbed by them from the atmosphere, causes decomposition into the tetrahalide and free tellurium.[4]

Telluric acid (H_2TeO_4, $2\,H_2O$).—There is no possibility of any other constitution for this acid (with molecules of water distinct from the anhydrous acid) except the graphic formula,

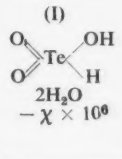
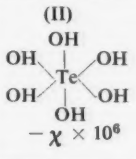


, $2H_2O$ (I)

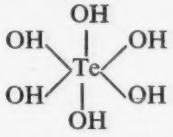
[3] Damiens, *Ann. Chim.*, 1923, **19**, 44.
[4] Brauner, *Monatsh*, 1889, **10**, 411.

Since it is a hydrated salt, it will be interesting to see how far the law of additivity applies to this case. The calculated and observed values are given under A of Table VI.

TABLE VI

Constitution	A (I)  $2H_2O$ $-\chi \times 10^6$	B (II)  $-\chi \times 10^6$
$(\chi_a)_1$	0·2855	0·2747
$(\chi_m)_1$	65·53	63·05
$(\chi_a)_2$	0·2757	0·2650
$(\chi_m)_2$	63·29	60·81
$(\chi_a)_3$	0·2850	0·2743
$(\chi_m)_3$	65·41	62·93
$(\chi_a)_4$	0·2751	0·2643
$(\chi_m)_4$	63·15	60·67
$(\chi_a)_E$	0·2508	0·2508
$(\chi_m)_E$	57·55	57·55

It is seen from the above that the calculated values are higher than the experimental ones. Gutbier[5] considers that both molecules of water in the hydrate H_2TeO_4, 2 H_2O are constitutional so that the formula for telluric acid would be H_6TeO_6 or $Te(OH)_6$ and the constitutional formula can be written as



(II)

The magnetic susceptibilities of telluric acid for the above constitution were calculated and are given under B of the above table.

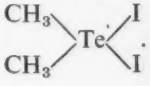
Even with the molecular constitution (II), the calculated values are higher than the observed ones, although they are a little lower than those

[5] Mellor's *Inorganic Chemistry*, **11**, 85.

calculated for (I). The experimentally determined value appears to be in line with the view of Ray Choudhary[6] who determined the magnetic susceptibility of a number of salts in the hydrated and anhydrous state and found that for a large number of substances investigated, the observed value for the hydrate is less than the calculated value. He also showed that the deviation from the additivity law is more prominent in cases where the heat of hydration is large. As a quantitative estimation he found that in the case of salts whose heats of hydration lie in the vicinity of 20 calories, the observed values of magnetic susceptibility are about 20 per cent. lower than the values calculated from the anhydrous salts. Though much importance cannot be attached to the quantitative nature of the change, the results on telluric acid support Ray Choudhary's general conclusions.

Varadachari[7] measured the diamagnetic susceptibilities of a number of crystalline inorganic salts. In the case of sodium sulphate[8] he found that the magnetic susceptibility of the hydrated salt undergoes no change when the salt is rendered anhydrous and he, therefore, suggested that the binding of the water molecules with the sulphate is very loose. It appears probable that the lowering in the observed value of telluric acid is due to the strong binding of the water molecules with oxygen ions. This conclusion is in agreement with the representation of the molecular constitution of the acid as $Te(OH)_6$.

International Critical Tables give the diamagnetic susceptibility χ_a for anhydrous telluric acid as $-0{\cdot}43\times10^{-6}$ and $\chi_m = -98{\cdot}69\times10^{-6}$. These values are very different from the calculated and the experimental ones and need correction.

Dimethyl tellurium diiodide $(CH_3)_2TeI_2$.—Pascal's additivity law is based mostly on his extensive results obtained from organic compounds, which have covalent bindings and as such his susceptibility constants fit in well in inorganic compounds involving covalent linkages, though complete agreement is not found as can be seen from the foregoing discussions. The study of some organo-inorganic compounds of tellurium was, therefore, undertaken. $(CH_3)_2TeI_2$ was selected because the nature of its covalency has been discussed at length by Lowry[9] and its graphic formula is fixed as  .

[6] *Zeit. Phys.*, 1932, **77**, 271.
[7] *Annamalai University Journal*, 1935, **4**, 73.
[8] *Proc. Ind. Acad. Sci.*, 1935, **2**, 161.
[9] *Soc. Chim. Belg.*, 1931, 91.

For the calculation of its susceptibility the value for iodine is taken as $-45{\cdot}6\times10^{-6}$.[10] The values for CH_3 calculated from different compounds are different, as shown below:—

Value for CH_3 from $CH_3Cl = -9{\cdot}86\times10^{-6}$
,, ,, ,, ,, $CH_3Br = -12{\cdot}78\times10^{-6}$
,, ,, ,, ,, $CH_3I = -11{\cdot}58\times10^{-6}$
,, ,, ,, ,, $CH_3OH = -16{\cdot}14\times10^{-6}$.

Consequently all the values for CH_3 were used, together with different values for tetravalent tellurium, to calculate the susceptibility of $(CH_3)_2TeI_2$.

TABLE VII

	χ calculated using CH_3 values from CH_3OH $-\chi\times10^6$	χ calculated using CH_3 values from CH_3Br $-\chi\times10^6$	χ calculated using CH_3 values from CH_3Cl $-\chi\times10^6$	χ calculated using CH_3 values from CH_3I $-\chi\times10^6$
$(\chi_a)_1$	0·3768	0·3606	0·3461	0·3547
$(\chi_m)_1$	154·97	148·25	142·40	145·85
$(\chi_a)_2$	0·3581	0·3420	0·3277	0·3362
$(\chi_m)_2$	147·40	140·68	134·84	138·28
$(\chi_a)_3$	0·3762	0·3600	0·3459	0·3542
$(\chi_m)_3$	154·83	148·11	142·27	145·71
$(\chi_a)_4$	0·3580	0·3415	0·3275	0·3358
$(\chi_m)_4$	147·26	140·54	134·70	138·14
$(\chi_a)_E$	..	..	..	0·3535
$(\chi_m)_E$	..	..	..	145·40
$(\chi_a)_{E_1}$	..	..	..	0·3600
$(\chi_m)_{E_1}$	..	..	..	148·10
$(\chi_a)_{O_1}$	0·3700	..	..	
$(\chi_m)_{O_1}$	152·20	..	..	

O_1 Refers to values calculated by Bhatnagar and Lahiri (*Curr. Sci.*, 1932, **1**, 380).
E_1 Refers to the experimental values of Bhatnagar and Lahiri (*loc. cit.*).

The above table clearly shows that the susceptibilities calculated by taking the value for CH_3 from CH_3I and the values of tetravalent tellurium according to Angus and Slater, are in very good agreement with the experimental values. The experimental value obtained by Bhatnagar and Lahiri[11] agrees very closely with that of the author. But their calculated value is rather high and may be due to the choice of the value of CH_3 which is large if

[10] Stoner, *Magnetism and Matter*, p. 468.
[11] *Ibid.*

calculated from CH_3OH. The author's calculated values in column 1 of the table is very nearly the same as that calculated by Bhatnagar and Lahiri.

Dimethyl tellurium dichloride ($CH_3)_2TeCl_2$.—This is the second organo-inorganic compound of tellurium selected for investigation. The following table gives the various values of the susceptibilities calculated in the same manner as in the case of $(CH_3)_2TeCl_2$.

TABLE VIII

	χ calculated using CH_3 values from CH_3OH $-\chi \times 10^6$	χ calculated using CH_3 values from CH_3Br $-\chi \times 10^6$	χ calculated using CH_3 values from CH_3I $-\chi \times 10^6$	χ calculated using CH_3 values from CH_3Cl $-\chi \times 10^6$
$(\chi_a)_1$	0·4737	0·4443	0·4336	0·4186
$(\chi_m)_1$	108·17	101·45	99·95	95·61
$(\chi_a)_2$	0·4403	0·4111	0·4005	0·3855
$(\chi_m)_2$	100·60	93·93	91·48	88·04
$(\chi_a)_3$	0·4729	0·4434	0·4330	0·4179
$(\chi_m)_3$	108·03	101·32	98·91	95·47
$(\chi_a)_4$	0·4403	0·4104	0·3999	0·3849
$(\chi_m)_4$	100·46	93·74	91·34	87·90
$(\chi_a)_E$	..	..	..	0·4047
$(\chi_m)_E$	..	..	..	92·43
$(\chi_a)_{E_1}$	..	..	..	0·42
$(\chi_m)_{E_1}$	..	..	..	95·92
$(\chi_a)_{O_1}$	0·47	..	..	
$(\chi_m)_{O_1}$	107·40	..	..	

O_1 Refers to the values calculated by Bhatnagar and Lahiri (*loc. cit.*).
E_1 Refers to their experimental values.

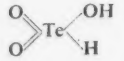
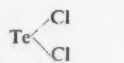
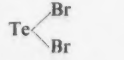
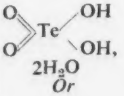
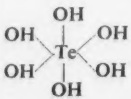
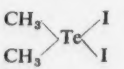
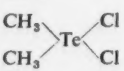
It is seen here also that if Slater's and Angus's values for Te^{++++} are employed, the only calculated values which approach the experimental ones are those in which the value for CH_3 obtained from CH_3Cl is used. The calculated value is widely different if the value for CH_3 obtained from CH_3I is employed. The experimental value of Bhatnagar and Lahiri is almost the same as that obtained by the author and their calculated value agrees with that given in column 1 of the above table. This is higher than the experimental value. This shows that for good agreement between the calculated and observed values the choice of the other radicals must be made from substances of similar nature.

Conclusion

All the results for the correct constitution have been summarised in Table IX.

TABLE IX

TABLE IX

Compound	Constitution	$-\chi \times 10^6$ observed by the author	$-\chi \times 10^6$ observed by other authors	$-\chi \times 10^6$ calculated by Slater's method	$-\chi \times 10^6$ calculated by the modification of Slater's method	$-\chi \times 10^6$ calculated by Angus's method	$-\chi \times 10^6$ calculated by the modification of Angus's method
H_2TeO_3 ..		(χ_a) 0·1966 (χ_m) 34·89	(χ_a) 0·24 (χ_m) 42·60 (Int. Crit. Tab.)	(χ_a) 0·1978 (χ_m) 35·12	(χ_a) 0·1852 (χ_m) 32·88	(χ_a) 0·1972 (χ_m) 35·00	(χ_a) 0·1844 (χ_m) 32·74
			(χ_a) 0·19 (χ_m) 33·72	(S. Meyer)			
			(χ_a) 0·2027 (χ_m) 35·97	Calculated by Bhatnagar and Luther.			
			(χ_a) 0·1897 (χ_m) 33·68	Calculated by Bhatnagar and Dhawan.			
$TeCl_2$ ..		(χ_a) 0·4760 (χ_m) 94·45		(χ_a) 0·4928 (χ_m) 97·83	(χ_a) 0·4057 (χ_m) 80·48	(χ_a) 0·4925 (χ_m) 97·70	(χ_a) 0·4471 (χ_m) 88·70
$TeBr_2$ ..		(χ_a) 0·3701 (χ_m) 106·2		(χ_a) 0·4121 (χ_m) 118·43	(χ_a) 0·3515 (χ_m) 101·08	(χ_a) 0·4117 (χ_m) 118·30	(χ_a) 0·3804 (χ_m) 109·30
H_2TeO_4, $2H_2O$ ..		(χ_a) 0·2508 (χ_m) 57·55	(χ_a) 0·43 (χ_m) 98·69 (Int. Crit. Tab.)	(χ_a) 0·2855 (χ_m) 65·53	(χ_a) 0·2757 (χ_m) 63·29	(χ_a) 0·2850 (χ_m) 65·41	(χ_a) 0·2751 (χ_m) 63·15
		(χ_a) 0·2508 (χ_m) 57·55		(χ_a) 0·2747 (χ_m) 63·05	(χ_a) 0·2560 (χ_m) 60·81	(χ_a) 0·2743 (χ_m) 62·93	(χ_a) 0·2643 (χ_m) 60·67
$(CH_3)_2TeI_2$..		(χ_a) 0·3535 (χ_m) 145·40		(χ_a) 0·3547 (χ_m) 145·85	(χ_a) 0·3362 (χ_m) 138·28	(χ_a) 0·3542 (χ_m) 145·71	(χ_a) 0·3358 (χ_m) 138·14
$(CH_3)_2TeCl_2$		(χ_a) 0·4047 (χ_m) 92·43		(χ_a) 0·4186 (χ_m) 95·61	(χ_a) 0·3855 (χ_m) 88·04	(χ_a) 0·4179 (χ_m) 95·47	(χ_a) 0·3849 (χ_m) 87·90

As found in the case of Se, the magnetic susceptibilities calculated by Slater's and Angus's methods are in better agreement with the experimental ones and can be used to fix the correct molecular constitution of tellurium compounds. It may be remarked here that in the case of organometallic compounds there is a better agreement between the calculated and experimental values than in the case of inorganic compounds. This finding is in agreement with the view put forward by Pascal and other workers.

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A PROPERTY OF INTEGRAL FUNCTIONS WITH REAL ROOTS AND OF ORDER LESS THAN TWO

By K. S. K. Iyengar

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I

Erdos and Grunwald* have proved the following theorem:—

Let $f(x)$ be a real polynomial, with real roots and let (1) $x = a_1$ and $x = a_2$ be consecutive single roots of $f(x)$, (2) Y, the height of the point of intersection of the tangents to the curve $y = f(x)$ at $(a_1, 0)$, $(a_2, 0)$ above the X-axis, (3) M the maximum of $|f(x)|$ in $(a_1\ a_2)$, then taking $a_1 < a_2$

$$\tfrac{8}{3}\,\mathrm{M}\,(a_2 - a_1) \geqslant \int_{a_1}^{a_2} |f(x)|\,dx \geqslant \tfrac{1}{3}\,|\,\mathrm{Y}\,|\,\cdot\,(a_2 - a_1). \qquad (1\cdot1)$$

It is the object of this paper to give four very comprehensive theorems which yield the best possible inequality [given as (3·3)] of the type (1·1). It will be obvious in the course of the paper that the inequality (1·1) is the best possible only in cases of symmetry. It may be noted that the method adopted here is quite different from that of Erdos, and Grunwald.

II. Statement of Theorems

Theorem (T_1): (1) Let $\phi(x)$, a real integral function, be defined by

$$\phi(x) = e^{\alpha x + \beta} \prod_1^{\infty} \left(1 - \frac{x}{a_n}\right) e^{\frac{x}{a_n}},$$

where α, β, $a_1, \cdots a_n \cdots$ are all real and $\Sigma \dfrac{1}{{a_n}^2}$ is convergent.

(2) Let $x = a_1$, $x = a_2$ $(a_1 < a_2)$ be consecutive single roots of $\phi(x) = 0$ and $\phi(x) > 0$ in $a_1 < x < a_2$.

* "On polynomials with real roots", in *Annals of Mathematics*, July 1939 (3), 537, **40**.

(3) $\phi'(a_1) = m_1$ and $\phi'(a_2) = -m_2$.

Then, if $A = \dfrac{\sqrt{m_1 m_2}}{a_2 - a_1} \cdot e^{-B\left(\frac{a_1 + a_2}{2}\right)}$ and $B = \log \dfrac{m_2}{m_1} \Big/ (a_2 - a_1)$

all the curves $Y = \phi(x)$ [where $\phi(x)$ satisfies conditions (2) and (3) and is of the type defined in (1)] in $a_1 \leqslant x \leqslant a_2$, lie above the minimum curve

$$Y = m(x) = A \cdot e^{Bx} \cdot (x - a_1)(a_2 - x) \tag{2·1}$$

and you can find real polynomials with real roots satisfying conditions (2) and (3) as near as you like to the minimum curve of (2·1).

THEOREM (T_2): Let $\phi(x)$ be a function satisfying conditions (1) and (2) of Theorem I and (3)′:—let $\phi(x)$ attain its maximum value in $a_1 \leqslant z \leqslant a_2$ at x_0 and $\phi(x_0) = M_0$.

Then all the curves $Y = \phi(x)$, [where $\phi(x)$ satisfies (1), (2) and (3)′], in $a_1 \leqslant x \leqslant a_2$ lie below the curve

$$Y = \bar{A}(x - a_1)(a_2 - x)\, e^{\bar{B} \cdot x} = M(x) \tag{2·2}$$

where $\bar{B} = \dfrac{2x_0 - a_1 - a_2}{(x_0 - a_1)(a_2 - x_0)}$ and $\bar{A} = \dfrac{M_0\, e^{-\bar{B}x_0}}{(x_0 - a_1)(a_2 - x_0)}$

and you can find the real polynomials with real roots satisfying (1), (2) and (3)′ as near as you like to the maximum curve of (2·2).

THEOREM (T_3): The curve $Y = m(x)$ of (2·1) (of Theorem T_1) lies above the parabola which touches the lines $Y = m_1(x - a_1)$, $Y = -m_2(x - a_2)$, at $(a_1, 0)$, $(a_2, 0)$ respectively. It coincides with it in case of symmetry, namely, $m_1 = m_2$.

THEOREM (T_4): The curve $Y = M(x)$ of (2·2) (of Theorem T_2) lies below the parabola passing through $(a_1, 0)$, $(a_2, 0)$ and touching the line $Y = M_0$ at $x = x_0$. If $x_0 = \dfrac{a_1 + a_2}{2}$, then the parabola will coincide with $Y = M(x)$.

III

From Theorems T_1 and T_3 we obtain

$$\int_{a_1}^{a_2} \phi(x)\, dx \geqslant \int_{a_1}^{a_2} m(x)\, dx = (a_2 - a_1)^2 \sqrt{m_1 m_2} \left\{ \frac{1}{6} + \frac{1}{2} \int_0^{B_1} \frac{u(\sinh u - u)}{B_1^{\,3}} \cdot du \right\}$$

$$\left[\text{where } B_1 = \frac{B(a_2 - a_1)}{2}, \text{ B being defined in (2·1)}\right]$$

$\geqslant$ Area of the parabola of contact (of Theorem T_3)† $= \frac{1}{3} \cdot Y(P) \cdot (a_2 - a_1)$. (3·1)

where Y (P) is the Y co-ordinate of P, the point of intersection of tangents at $(a_1, 0)$ $(a_2, 0)$ to the curves $Y = \phi(x)$.

From Theorems T_2 and T_4 we get,

$$\int_{a_1}^{a_2} \phi(x)\, dx \leqslant \int_{a_1}^{a_2} M(x)\, dx = \frac{e^{\frac{-2u_0^2}{1-u_0^2}}}{1-u_0^2} \cdot 2 M_0 (a_2 - a_1) \cdot \int_0^{B_2} \frac{u \sinh u}{B_2^3} \cdot du$$

$$\left[\text{where} \quad u_0 = \frac{2x_0 - a_1 - a_2}{a_2 - a_1} \quad \text{and} \quad B_2 = \frac{2u_0}{1-u_0^2}\right]$$

$$\leqslant \text{Area of the parabola of (Theorem } T_4)\ddagger = \frac{2 M_0}{3} (a_2 - a_1) \qquad (3 \cdot 2)$$

so that combining (3·1) and (3·2), if $\phi(x)$ satisfies (1), (2), (3) and (3)′ we obtain

$$\frac{2}{3} M_0 (a_2 - a_1) \geqslant 2 M_0 (a_2 - a_1) \cdot \frac{e^{\frac{-2u_0^2}{1-u_0^2}}}{1-u_0^2} \cdot \int_0^{B_2} \frac{u \cdot \sinh u}{B_2^3}\, du \geqslant \int_{a_1}^{a_2} \phi(x)\, dx \geqslant$$

$$\geqslant \sqrt{m_1 m_2}\, (a_2 - a_1)^2 \left\{\frac{1}{6} + \frac{1}{2} \int_0^{B_1} \frac{u(\sinh u - u)}{B_1^3} \cdot du\right\} \geqslant \tfrac{1}{3} Y(P) \quad (a_2 - a_1). \quad (3 \cdot 3)$$

It will be obvious from the proofs of Theorems T_3 and T_4 that equality sign can occur in the first and last inequality signs in (3·3), only in case of symmetry, *i.e.*, $m_1 = m_2$ and $x_0 = \frac{a_1 + a_2}{2}$.

Note.—Generalization of Theorem T_1 is possible to the case where conditions (2) and (3) may be replaced by

$(2)_1$ $\phi(a_1) = 0$ a zero of q_1th degree and $\phi(a_2) = 0$ of q_2th degree and $\phi(x) > 0$ in $a_1 < x < a_2$.

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†, ‡ The following two elementary propositions are implied :

(1) If $Y = P(x)$ be a parabola touching the lines $Y = m_1 (x - a_1)$ and $Y = -m_2 (x - a_2)$ at $(a_1, 0)$, $(a_2, 0)$ respectively, then $\int_{a_1}^{a_2} P(x)\, dx = \frac{1}{3} Y(P)(a_2 - a_1) = \frac{m_1 m_2}{m_1 + m_2} \cdot \frac{(a_2 - a_1)^2}{3}$.

(2) If $Y = P(x)$ a parabola passes through $(a_1, 0)$ and $(a_2, 0)$ and touches $Y = M_0$ at $x = x_0$ then $\int_{a_1}^{a_2} P(x)\, dx = \frac{2}{3} M_0 (a_2 - a_1)$.

$(3)_1$ $\phi^{(q_1)}(a_1) = m_1$ $\phi^{(q_2)}(a_2) = \{(-1)^{q_2}\} m_2$. Then the minimum curve will be of the type $Y = A(x-a_1)^{q_1} (a_2 - x_1)^{q_2} e^{B \cdot x}$ in $a_1 \leqslant x \leqslant a_2$.

A and B being expressible in terms of m_1 m_2, a_1, a_2 q_1 q_2.

similar generalization for Theorem T_2 is possible.

Proof of Theorem (T_1): Let $m(x)$ be the function defined in (2·1) and $\phi(x)$ the function satisfying (1), (2) and (3).

Let $F(x) = \dfrac{\phi(x)}{m(x)}$. Then from condition (3) of Theorem T_1

$$F(a_1) = F(a_2) = 1 \tag{4·1}$$

and from condition (1) of Theorem T_1 we obtain

$$\frac{d^2}{dx^2} \log F(x) = -\sum_{n=3}^{\infty} \frac{1}{(x-a_n)^2} = -\mu(x), \tag{4·2}$$

where all the a_n's for $n \geqslant 3$ lie outside the interval $a_1 \leqslant x \leqslant a_2$ by condition (2). Since $\log F(a_1) = \log F(a_2) = 0$, we can easily prove

$$\text{Log } F(x) = \frac{(x-a)_1 \ (a_2 - x)}{\underline{|2}} \mu(\xi), \text{ where } a_1 < \xi < a_2 \tag{4·3}$$

so that $\log F(x) \geqslant 0$, equality occurring only when $F(x) \equiv 1$ so that

$$\phi(x) \geqslant m(x). \tag{4·4}$$

To prove the latter half of the theorem, we assume without any loss of generality $a_1 = -1$, $a_2 = +1$ and let $m(x)$ stand for the corresponding minimum function of (2·1).

Let $P(x)$ be defined by $P(x) = D(1-x^2)\left(1-\dfrac{x}{a}\right)^n$ (4·5)

D, and a, to be suitably chosen such that $|a| > 1$ and $P'(1) = -m_2$, $P'(-1) = m_1$.

Since $P'(x) = -2Dx\left(1-\dfrac{x}{a}\right)^n + (1-x^2) \cdot D \cdot \{\cdot\ \cdot\} \cdot$ and $P'(1) = -m_2$,

$$P'(-1) = m.$$

We obtain $$D\left(1-\frac{1}{a}\right)^n = \frac{m_2}{2}, \quad D\left(1+\frac{1}{a}\right)^n = \frac{m_1}{2}$$

so that $$a = \frac{\left(\dfrac{m_1}{m_2}\right)^{\frac{1}{n}} + 1}{\left(\dfrac{m_1}{m_2}\right)^{\frac{1}{n}} - 1} \quad \text{if } m_1 \neq m_2. \tag{4·6}$$

Let $m_1 > m_2$ (argument being of the same type when $m_2 > m_1$)

and let $\theta(x) = \log \dfrac{P(x)}{m(x)}$.

Then $\theta(\pm 1) = 0$ and $\theta''(x) = -\dfrac{n}{(x-a)^2}$

and if $-1 \leqslant x \leqslant 1$ $0 \leqslant \theta(x) \leqslant \frac{1}{2}(1-x^2)$. [Max. of $-\theta''(x)$ in $(-1, 1)$] since $m_1 > m_2$, $a > 1$

and Max. of $-\theta''(x)$ will be $\dfrac{n}{(1-a)^2} = \dfrac{n}{4}\left\{\left(\dfrac{m_1}{m_2}\right)^{\frac{1}{n}} - 1\right\}^2$ (4·7)

and will be of order $0\left(\dfrac{1}{n}\right)$ for large n

so that for large n, $P(x) = m(x) \cdot e^{0\left(\frac{1}{n}\right)}$ or $|P(x) - m(x)| \leqslant 0\left(\dfrac{1}{n}\right)$ in $|x| \leqslant 1$. (4·8)

In case $m_1 = m_2$, $m(x)$ itself will be a quadratic, thus proving the latter half of Theorem T_1.

Proof of Theorem T_2: Let $M(x)$ be the function defined in (2·2) and $\phi(x)$ the function satisfying conditions (1), (2) and (3)′, and let

$$F(x) = \log \frac{\phi(x)}{M(x)}.$$

Then from condition (3)′ we obtain $F(x_0) = F'(x_0) = 0$ (4·9)

and from condition (1) $\dfrac{d^2}{dx^2} F(x) = -\sum_3^\infty \dfrac{1}{(x-a_n)^2} \cdot = -\mu(x)$, (4·10)

where all a_n's for $n \geqslant 3$ lie outside $a_1 \leqslant x \leqslant a_2$

Now $F(x) = F(x_0) + (x - x_0) F'(x_0) - \dfrac{(x-x_0)^2}{\underline{|2}} \cdot \mu(\xi)$

$$= -\frac{(x-x_0)^2}{\underline{|2}} \cdot \mu(\xi) \quad \text{for } a_1 \leqslant x \leqslant a_2 \tag{4·11}$$

ξ being in the interval (x_0, x).

Now $\mu(x) > 0$ in $a_1 \leqslant x \leqslant a_2$

so that $F(x) \leqslant 0$ in $a_1 \leqslant x \leqslant a_2$

equality occurring only when $F(x) \equiv 0$.

i.e., in $a_1 \leqslant x \leqslant a_2$ $M(x) \geqslant \phi(x)$. (4·12)

The latter half of the Theorem T_2 can be proved in the same manner as the corresponding part of Theorem T_1.

Proof of Theorem T_3: Without loss of generality we take $a_1 = -1$, $a_2 = +1$, given $m_2 \neq m_1$, the parabola of contact will be given by

$$Y = \sqrt{\alpha^2 + \beta^2 + 2\alpha\beta x} - \alpha - \beta x = P(x) \quad \text{in } -1 \leqslant x \leqslant 1$$

where $$\alpha = \frac{2 m_1 m_2 (m_1 + m_2)}{(m_1 - m_2)^2} \qquad \beta = \frac{2 m_1 m_2}{m_1 - m_2}. \tag{4·13}$$

Let $F(x) = \log \frac{m(x)}{P(x)}$. Then since $\frac{1}{P(x)} = \frac{\sqrt{\alpha^2 + \beta^2 + 2\alpha\beta x} + \alpha + \beta x}{\beta^2 (1 - x^2)}$

$$F(x) = \log \frac{m(x)}{\beta^2 (1 - x^2)} + \log \{\sqrt{\alpha^2 + \beta^2 + 2\alpha\beta x} + \alpha + \beta x\}$$

$$= \quad ,, \quad + \log \theta(x) \tag{4·14}$$

Now $$F(\pm 1) = 0 \text{ and } \frac{d^2}{dx^2} F(x) = \frac{d^2}{dx^2} \log \theta(x) = \frac{\theta''}{\theta} - \frac{(\theta')^2}{\theta^2}$$

$$\text{and} \quad \theta'' = - \frac{(\alpha\beta)^2}{(\alpha^2 + \beta^2 + 2\alpha\beta x)^{\frac{3}{2}}}. \tag{4·15}$$

Since $\theta > 0$ and $\theta'' < 0$ in $|x| \leqslant 1$

$$\frac{d^2}{dx^2} F(x) < 0 \quad \text{in } |x| < 1. \quad \text{Let} - \mu(x) = \frac{d^2 F}{dx^2}.$$

Then if $|x| \leqslant 1$ $\qquad F(x) = \left(\frac{1 - x^2}{2}\right) \cdot \mu(\xi) \quad -1 < \xi < 1$

Hence $$F(x) > 0 \qquad \text{in } |x| < 1$$

or $$m(x) > P(x) \quad \text{in } |x| < 1. \tag{4·16}$$

In case $m_1 = m_2$ the parabola of contact will be defined

$$\text{by} \qquad Y = \frac{m_1}{2}(1 - x^2) \tag{4·17}$$

and coincides with $Y = m(x)$ the minimum curve of (2·1).

Proof of Theorem T_4: As in Theorem T_3 we take $a_1 = -1$, $a_2 = +1$. Let $x_0 \neq 0$. Then the parabola passing through $(\pm 1, 0)$ and touching $Y = M_0$ at x_0 will be

$$Y = \sqrt{\alpha^2 + \beta^2 + 2\alpha\beta x} - \alpha - \beta x = P(x)$$

where $$\alpha = \frac{M_0}{2 x_0^2} \qquad \beta = - \frac{M_0}{x_0} \tag{4·18}$$

and let $$F(x) = \log \frac{M(x)}{P(x)}.$$

Then $$F(x_0) = F'(x_0) = 0$$

and arguing as in Theorem T_3 we prove

$$F''(x) < 0 \quad \text{in} \quad -1 \leqslant x \leqslant 1 \tag{4·19}$$

and as in Theorem T_2 for x in $-1 \leqslant x \leqslant 1$, $F(x) < 0$ when $x \neq x_0$,

i.e., $$M(x) < P(x) \quad \text{when } x \neq x_0$$

$$= P(x) \quad \text{for} \quad x = x_0, \quad -1 \leqslant x \leqslant 1. \tag{4·20}$$

In case $x_0 = 0$ the parabola will be $Y = M_0(1 - x^2)$ and coincides with the maximum curve of (2·2). (4·21)

STUDIES ON THE DEPENDENCE OF PHYSIOLOGICAL ACTION ON CHEMICAL CONSTITUTION

Part I. Difference in Odour of *d*-, *l*-, and *dl*- Derivatives of Amino- and Bisamino- Methylenecamphors

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It is well known that optically active isomers, despite the fact that they are identical in chemical structure, differ from one another in physical properties of a vectorial (directional) nature, such as, for example, direction of rotation of the plane of polarised light, unsymmetrical distribution of the hemihedral facets in their crystal forms and also in the enantiomorphous distribution of pyro- and piezo- electrical polarity. The magnitude of the vectorial properties is, however, identical for the enantiomorphous forms. The optically active and opposite forms also differ in their biological action on micro-organisms, and enzymes. The question that they may have different physiological and pharmacological action on higher organisms was later studied. In 1886 Piutti[1] observed that *d*-asparagine had a sweet taste, whereas the naturally occurring *l*-asparagine was insipid. Other amino acids behaved in the same way. Cushny[2] found that *l*-hyoscyamine was twice as powerful in paralysing the vagus as the racemic form, atropine, while the *d*-form was twenty times weaker in this action. The naturally occurring *l*-nicotine, from tobacco, is much more powerful in its action on animals than the *d*-nicotine, which has only a mild and temporary action. Natural adrenalin, which is *lævo*-rotatory, has a marked constricting effect on the blood vessels and is used in the form of subcutaneous injections for arresting bleeding. It was found by Cushny to be 12 to 15 times more active than *d*-adrenalin. Similar differences have been noted for ephedrine and other drugs. One of the most striking examples of different physiological action recently observed is vitamin C or ascorbic acid[3]: the dextro-rotatory acid is active, the *lævo*-form being physiologically inactive.

These differences in the physiological action of the optically active and their racemic forms are also associated with other properties, such as, odour. J. von Braun[4] has noted a few cases in which he observed differences in odours

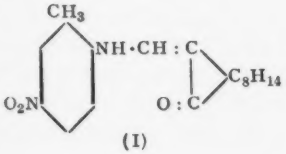
among the optically active and racemic forms. Thus in the case of γ η-dimethyloctanols, he found that the odour of the optically active alcohol was more refreshing and penetrating than that of its inactive isomeride, but in the case of *m*-methylcyclohexylethylene oxide, the racemic form had an intenser and sharper odour than the active form. The optically active dimethylcyclohexanols have sweeter odours: the odour of the *d*-form is fresher and more powerful while that of the *l*-variety is milder and heavier.

In a preliminary communication[5] we recorded a few instances of differences in odours among the optically active and racemic forms of substances which are derivatives of amino- and bisamino-methylenecamphors. They have already been described by us.[6] The odour of these substances was observed by different observers and the order of the intensity of odour as noticed by them was *l*- > *dl*- > *d*- in the four series of compounds given in the following table :—

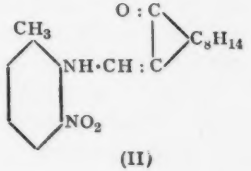
Name of the compound	Order of intensity of odour	Number of observers
5·Nitro-*o*-toluidinomethylene-camphors I	l > dl > d	10
3·Nitro-*o*-toluidinomethylene-camphors II	l > dl > d	13
2:5-toluylenebisaminomethylene-camphors III	l > dl > d	11
2:3-toluylenebisaminomethylene-camphors IV	l > dl > d	11

The colour and odour of the racemic form of 3·nitro-*o*-toluidino-methylenecamphor resemble those of saffron; the odours of the *dextro*- and *lævo*-isomerides of this substance as well as of the remaining compounds in the above table which have not been identified with those of any known substance, are pleasant.

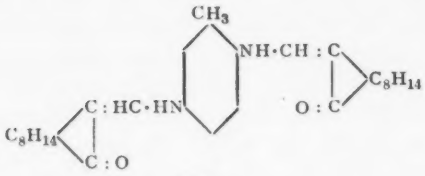
The position of the nitro group in the nitro-*o*-toluidino-methylene-camphors has a marked effect on the intensity of their odours : the odour of the dyes with the nitro group in the 3-position (II) are more intense than those of the corresponding forms with the nitro group in the 5-position (I):—



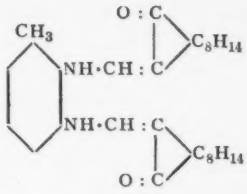
(I)



(II)



(III)



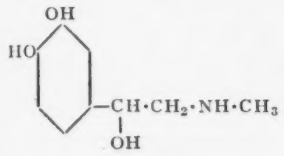
(IV)

Numerous hypotheses have been put forward to account for the different physiological activities of optically active isomers. Pasteur[7] explained such differences in action by supposing that the nerve-substances and the tissue-substances of the animals are themselves asymmetric. They, therefore, react differently towards the right- and left-handed forms of physiologically active forms. The difference in action, according to Pasteur, is therefore chemical.

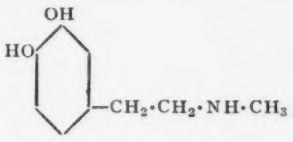
Porter and Ihrig[8] were able to effect separation of racemic dyestuffs into their optically active components by differential adsorption of one of the isomers by wool. King[9] arguing from these observations, attributed the difference in the physiological action of optically active forms to physical rather than chemical causes. Erlenmayer[10] attributed the difference in physiological action to some unknown force or "asymmetric affinity" which favoured the reaction of one optical isomer in preference to that of the other. Cushny (*ibid.*, p. 58) in reviewing these theories stated that none of them afforded an adequate explanation and concluded " that here some chemical combination occurs of such a nature that the isomers no longer form mirror images and these therefore differ in their physical properties and reactions". Cushny did not, therefore, assume that the optically active substances of cells reacted preferentially with one of the optically active forms of the physiologically active compound ; he rather favoured the view that the occurrence of identical reactions gives rise to substances with different physical and therefore also of physiological properties.

Easson and Stedman[11] have suggested a novel and interesting explanation: they assume that there is no difference in the causes which produce different activity of optical isomers on the one hand and the causes of the different activity of structural isomers on the other. Their hypothesis is as follows:--In a compound containing an asymmetric carbon atom, in which the four different radicals are arranged at the four corners of the tetrahedron, three active radicals lying in a plane formed by one of the faces of the tetrahedron can only come into close combination with the specifically active " receptors" of end organs when these are similarly arranged. In the enantiomorphous arrangement of the radicals in the opposite active form, only two

out of the three groups concerned can come into close proximity with their receptors. Consequently the more weakly active isomer behaves physiologically as if one of the active groups was absent. In support of their hypothesis, they cite, among others, the following example : the pressor activity of *d*-adrenalin is 12 to 15 times smaller than that of *l*-adrenalin and equals that of 3 : 4-dioxy-phenylethylmethylamine, which lacks the alcoholic hydroxyl group in the side chain of adrenalin as shown in the following formulæ :



adrenalin



3 : 4-dioxy-phenylethylmethylamine

Similarly it may be inferred that the different odours of the optical isomers may be brought about by the two different arrangements of the active groups of the enantiomorphs in juxtaposition with the specific receptors of the nerve-substances of the cells of the olfactory organs. In one of these arrangements, one of the physiologically active groups is absent, thus producing different odours.

The present writers further suggest that there is a great similarity in the theory of Easson and Stedman in accounting for the different physiological activities of the optically active isomers on the one hand and the hypothesis of Werner[12] in explaining the occurrence or non-occurrence of " Walden Inversion" on the other. Easson and Stedman assume that one of the three groups contained in one of the faces of the tetrahedron, representing the asymmetric carbon atom, gets locked into the cell mechanism of the organism by its specific " receptors", which is shown in the increased physiological activity of the isomer. In the enantiomorph, the juxtaposition of this particular group with and locking into the " receptors" is lacking and consequently it behaves more weakly in its physiological action. According to Werner, the substitution of a group x in an asymmetric carbon compound , takes place in one of the two following ways :—If the new substituent group comes in juxtaposition with one of the three faces of the tetrahedron containing the group x, then as a result of substitution no "Walden Inversion" occurs. If, on the other hand, the new group is attracted towards the fourth face of the tetrahedron, which does not contain the group x, then a " Walden Inversion" takes place. There is a further similarity in the two hypotheses, namely, that they cannot predict the effect beforehand. This is, therefore,

a weak point which militates against the theories both of Werner, regarding the " Walden Inversion" and Easson and Stedman in predicting which of the two optical isomers will be physiologically stronger.

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